TITLE

STUDIES OF 1,2-NAPHTHOQUINONE MONO-OXIMATO COMPLEXES

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by

YUSUF MUSA

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Inco (Europe) Ltd

July 1991

To Sarah

Like all young men I set out to be a genius
but, mercifully laughter intervened

Clea Lawrence Durrell

DECLARATION

Whilst registered as a candidate for this degree the author has not been registered as a candidate for any other award.

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YUSUF MUSA

STUDIES OF 1,2-NAPHTHOQUINONE MONO-OXIMATO COMPLEXES

ABSTRACT

The synthesis of 1,2-naphthoquinone 1-oxime and 1,2-naphthoquinone 2-oxime complexes of rhodium and iridium has been investigated. In the case of rhodium, complexes of the type $Rh(1\text{-nqo})_3$ have been prepared by reacting 1,2-naphthoquinone 1-oxime with hydrated rhodium(III) chloride. Both products were obtained as mixtures of isomers. The interaction of 1,2-naphthoquinone 2-oxime with rhodium(III) chloride yielded $Rh(2\text{-nqo})_3$ also as a mixture of isomers. The trichelates were also obtained from the nitrosation of the appropriate naphthol in the presence of rhodium(III) chloride. In contrast, the corresponding reaction systems involving iridium gave very complex mixtures involving both iridium containing species and organic products. One of the iridium products, $[pyH][Ir(1\text{-nqo})Cl_3 py]$, has been isolated in the pure state and characterised by X-ray crystallography. The complexes $Ir(1\text{-nqo})_3$ and $Ir(2\text{-nqo})_3$ were also isolated but in low yields.

All trichelates were shown to be diagmagnetic. None reacted with either pyridine or triphenylphosphine. These observations have been rationalised in terms of crystal field stabilisation energy. The behaviour of the rhodium and iridium complexes towards the Lewis bases contrasts that of analogous iron and cobalt complexes. The X-ray study of $[pyH][Ir(1\text{-nqo})Cl_3 py]$ has shown that the ligand is chelated to the metal as been observed in first transition series metal complexes derived from such ligands.

The use of 1,2-naphthoquinone 1-oxime as a potential ligand for separating rhodium from iridium has been investigated. Optimum conditions for the separation and recovery of rhodium was established. This was evaluated as a technique for refining rhodium and iridium in the current process at Inco (Europe) Ltd.

The synthesis of cobalt, rhodium, copper, iron and nickel complexes of 1,2-naphthoquinone 1-oxime-3,6-disulphonic acid ($nRsH_3$) has been investigated and the complexes were isolated in solid form by developing a separation technique. Cobalt(III) and rhodium(III) salts reacted with the ligand to give metal complexes of type $M(nRs\ Na)_3$. The behaviour of the 1,2-naphthoquinone 1-oxime-3,6-disulphonic acid towards iron(II) and iron(III) or copper salts was shown to be more complex and interesting than previously reported. Both iron(II) and iron(III) chloride gave an iron(II) product of the type $Fe(nRs\ Na)$ whilst iron(II) ammonium sulphate gave an Fe(II) product of the type $Fe(nRs\ Na)_2$. The nickel salts gave a complex containing two ligands per metal, $Ni(nRsHNa)_2$.

The complexes of iron(II) and copper(II) of 1,2-naphthoquinone 1-oxime-3,6-disulphonic acid catalysed aerobic oxidation of catechols. The oxidation involved oxidative cleavage of the aromatic ring of catechol by molecular oxygen to give muconic acid anhydride and 2H-pyran-2-one in addition to benzoquinone. This behaviour is very similar to enzyme catalysed oxygenation.

ACKNOWLEDGEMENTS

I would like to express my sincere thanks to my supervisor, Professor John Charalambous, for his guidance, patience and encouragement throughout the course of this work.

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ABBREVIATIONS

1-nqoH	1,2-Naphthoquinone 1-oxime
2-nqoH	1,2-Naphthoquinone 2-oxime
5-MeOqoH	5-Methoxy quinone 1-oxime
4-ClqoH	4-Chloroquinone 1-oxime
4-MeqoH	4-Methylquinone 1-oxime
4-BuqoH	4-tert-Butylquinone 1-oxime
qoH	1,2-Quinone mono-oxime
$nRsH_3$	1,2-Naphthoquinone 1-oxime-3,6-disulphonic acid
$nRsHNa_2$	1,2-Naphthoquinone 1-oxime-3,6-disulphonic acid, disodium salt
SalenH	Bis(salicylidene)ethylenediamine
Saldpt	N,N' -(3,3'-dipropylamine)bis(salicylideneaminato)
Bpy	Bipyridine
dmgH	Dimethylglyoxime
tpp	Tetraphenylporphin
Ph_3P	Triphenylphosphine
TBP	Tributylphosphate
hfacH	Hexafluoroacetylacetone
acacH	Acetylacetone
en	Ethylenediamine
py	Pyridine
oxa	Oxalic acid
DTBC	Di-tert-butylcatechol
tlc	Thin layer chromatography
glc	Gas liquid chromatography
ir	Infra-red chromatography
uv/vis	Ultra-violet/visible
FAB	Fast atomic bombardment
AAS	Atomic absorption spectrophotometry

CONTENTS

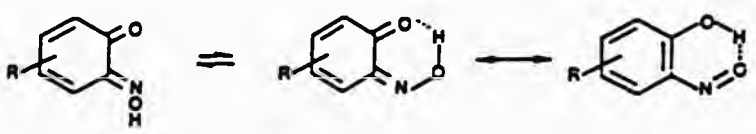
CHAPTER ONE

1,2-QUINONE MONO-OXIMES AND THEIR METAL COMPLEXES

1.1 Introduction

1,2-Quinone mono-oximes, their derivatives and their metal complexes pose some interesting structural problems and have shown considerable promise as substrates in synthesis and as catalysts. The complexes have also found other useful applications, e.g. as dyes. The chemistry of these compounds has recently been the subject of extensive investigations both within these laboratories and elsewhere.

It is well known that 1,2-quinone mono-oximes (1.1 and 1.2) can tautomerise to the corresponding 2-nitrosophenols (1.3) and the nomenclature may often appear confusing.



1.1 1.2 1.3

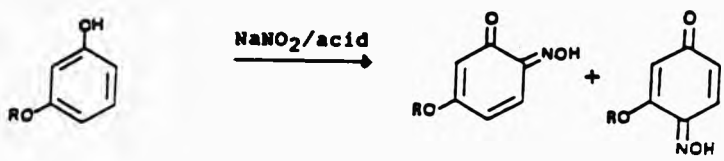
Throughout this thesis both the terms nitrosophenol and quinone mono-oxime will be used, but this does not necessarily mean that the compound described possesses

that particular structure, or exists in that form, unless specifically mentioned.

1.2 1,2-Quinone mono-oximes

1.2.1 Preparation of 1,2-quinone mono-oximes

When treated with sodium nitrite and dilute aqueous acid, phenols usually form 1,4-benzoquinone mono-oximes as the major products.[1] However, when resorcinol or 3-alkoxyphenols are used, the 2-substituted isomers are also obtained (Reaction 1.1).[2]



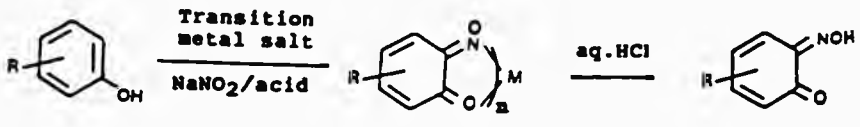
[R = H or alkyl]

(Reaction 1.1)

In the case of 1-naphthol, the nitrosation with nitrous acid gives mainly the 1,2-naphthoquinone 2-oxime and a small amount of the 1,4-naphthoquinone 4-oxime.[3] On the other hand, 2-naphthol gives only 1,2-naphthoquinone 1-oxime.

Other methods for the preparation of 1,2-quinone mono-oximes have been reported. These methods include the action of hydroxylamine on a quinone,[4,5] sodium hydroxide on certain nitro-aromatic compounds[6] or

boiling nitrosaniline in the presence of potassium hydrogen sulphate.[7] When a phenol or naphthol is nitrosated in the presence of a transition metal salt, a metal complex of 1,2-quinone mono-oxime results.[8,9] The function of the metal salt, according to some authors, is to ensure the attack on the 2-position of the 1,2-quinone mono-oxime. Subsequent acidification of the complex provides the free 1,2-quinone mono-oxime (Reaction 1.2). However, the formation and isolation of 1,2-quinone mono-oxime from its complex must be viewed with scepticism as experimental detail is generally lacking and no analytical data for the products have been provided.



(Reaction 1.2)

Another method used in the preparation of certain 1,2-quinone mono-oximes involves the acidification of their alkali metal complexes. These complexes are obtained by the reaction of a phenol with amyl nitrite and an alkali metal hydroxide or alkoxide in ethanol. For example, 1,3-dihydroxybenzene is used to prepare 5-hydroxy-1,2-benzoquinones mono-oxime.[10]

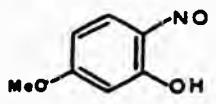
1.2.2 Properties of 1,2-quinone mono-oximes

The fact that 4-nitrosophenols have a pronounced tendency to tautomerise to the corresponding 1,4-quinone mono-oximes has long been recognised.[11-13] 1,4-Benzoquinone mono-oxime has been isolated in two forms. One conformation crystallises from hot water and is colourless and the other form is obtained by recrystallisation from acetone as yellow needles. The latter form was shown to be identical with the mono-oxime of 1,4-benzoquinone, which was prepared by the action of hydroxylamine on 1,4-benzoquinone. Consequently, the colourless form was formulated as 4-nitrosophenol. Several workers have shown that in solution, a tautomeric equilibrium involving the 4-nitrosophenol and 1,4-benzoquinone mono-oxime forms exists (Reaction 1.3).[14-16]

(Reaction 1.3)

This type of nitrosophenol-quinoneoxime tautomerism is also shown by 1,2-quinone mono-oximes. For example, in the case of 5-methoxy-1,2-benzoquinone 2-oxime, a green form is obtained by recrystallising the compound

from benzene and a brown form by crystallisation from ethyl alcohol.[17] The two forms have different melting points. Furthermore the green form transforms into the brown form slowly on heating. The green form was assigned the phenolic structure (1.4) and the brown form the quinoneoximic structure (1.5).



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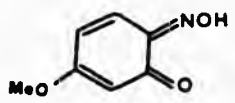
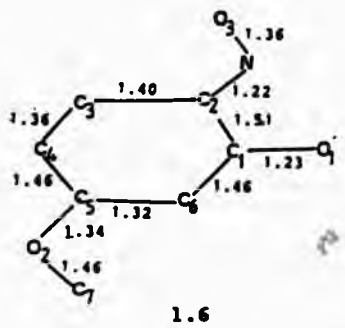


1.5

Similar suggestions were put forward for several other 1,2-quinone mono-oximes, e.g. β-5-(2-chloroethoxy)-1,2-benzoquinone 2-oxime,[18] 5-n-propoxy-1,2-benzoquinone 2-oxime.[19] These suggestions are only partially correct, since in addition to the quinone oxime-nitrosophenolic tautomerism, there is also the possibility of geometrical isomerism in the oximic form.

X-ray crystallographic studies of the red form of 5-methoxy-1,2-benzoquinone 2-oxime (1.6)[20] and the green form of 5-n-propoxy-1,2-oxime (1.7) indicate that both have quinone-oximic structures.[19]



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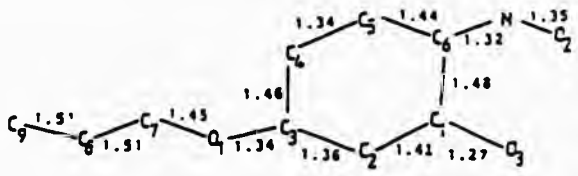
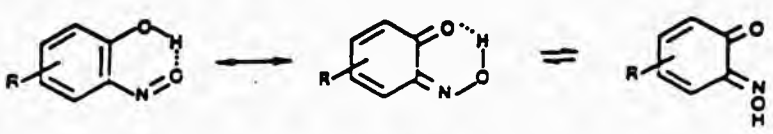


1.7

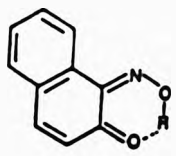
In the red form of 5-methoxy-2-benzoquinone 2-oxime (1.6), the C-C bonds are not equal and the C_2-N and C_1-O_1 bonds have a profound double bond character. This is essentially an indication of quinone oxime structure, with the NOH group bent away from the quinoid oxygen. This is assigned the anti-oxime structure, a feature which influences intermolecular hydrogen bonding.[20]

In the case of 5-n-propoxy-1,2-benzoquinone 2-oxime the X-ray studies have shown that the oximic oxygen is bent towards the quinoid oxygen. This is a syn-oxime arrangement and the compound exhibits intramolecular hydrogen bonding (1.7).[20] In solution, it has been shown that a tautomeric equilibrium exists which is solvent-dependent.[21,22] Thus the nitrosophenol-quinoneoxime system can be best represented as shown in Scheme 1.1, which is presented again below for the convenience of the reader.



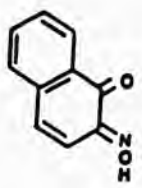
Scheme 1.1

In the case of 1,2-naphthoquinone 1-oxime, only one form has been isolated. On the basis of infra-red and nuclear magnetic resonance spectroscopy, it has been suggested that the compound has a syn-quinone oximic structure and the contribution from the nitrosophenolic structure is minimal. The infra-red spectrum of 1,2-naphthoquinone 1-oxime contains sharp bands at 1618, 1526, 1075, cm^{-1} and a broad weak band at 2700 cm^{-1}. On the basis of an extensive study of solid and solution spectra of related compounds, these bands have been assigned to νC=O, C=N, N=OH and OH respectively. Furthermore the presence of intramolecular hydrogen bonding has been proposed (1.8).[23]



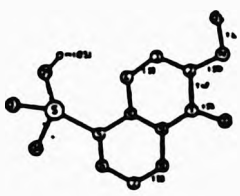
1.8

In the case of 1,2-naphthoquinone 2-oxime again only one form has been isolated. The infra-red spectrum of this compound contains sharp bands at 3210, 1668, 1550 and 1069 cm^{-1} which have been assigned to νOH, C=O, C=N, and N=OH respectively and intermolecular hydrogen bonding has been suggested (1.9). Some further support for this



1.9

suggestion has been provided by a recent X-ray crystallographic study of its 5-sulphonated derivative which shows the oxygen of the NO group to be on the opposite side of the ring oxygen (1.10).[24]



1.10

1.2.3 Complex formation

1,2-Quinone mono-oximes and their derivatives afford strong, highly coloured complexes readily that are useful in metal ion separation and analysis.[25,26]

The formation of a 1,2-quinone mono-oximato metal complexesinvolves the replacement of the acidic proton by

the metal in the 1,2-quinone mono-oxime tautomeric system (Scheme 1.1).

Intensive work has recently been carried out on the study of metal complexes derived from 1,2-quinone mono-oximes.[27-31] Most metal ions of the first transition series have been used to prepare complexes with 1,2-quinone mono-oximes and 1,2-naphthoquinone mono-oximes. Some reported complexes of quinone oximes of transition metals are presented in Table 1.1. The metal ions are usually chelated by the anionic ligand through the nitrogen atom of the oxime group and the quinoid oxygen. In the actinide complexes diaquobis (1,2-naphthoquinone-1-oximato)dioxouranium(VI) (triphenyl phosphine oxide) and diaquobis(1,2-naphthoquinone-2-oximato) dioxo-uranium(VI)trichloromethane dioxouranium(VI), only the oxime group is involved in the bonding of the anionic ligand to the metal.[32] There are also some examples of metal complexes in which the 1,2-quinoneoximes are present as neutral or protonated species.[33,34] For example, $(1\text{-nqoH})_2FeCl_2$ [33] and $[qoH_2]_2[CuCl_4]$ (qoH = 4-chloro-1,2-benzoquinone 2-oxime).[29]

1.2.4 Preparation of quinone mono-oxime complexes

Several methods have been employed for synthesising 1,2-quinone mono-oximes complexes and can be classified into the following groups: i) the direct method, ii) the nitrosation method, iii) the metal carbonyl method and iv) the ligand exchange.

Table 1.1 Some metal complexes of 1,2 quinone mono-oxime

1,2 Quinone mono-oxime	Metal (ox. state)	Complex	Ref.
5-MeOqoH	Fe(III)	$Fe(qo)_3$	24
	Cu(II)	$Cu(qo)_2$	29
5-MeOqoH	Ni(II)	$Ni(qo)_2$	35
4-ClqoH	Ni(II)	$Ni(qo)_2$	31
	Ni(II)	$K[Ni(qo)_3](CH_3)_2CO$	35
	Cu(II)	$Cu(qo)_2$	29
4-MeqoH	Ni(II)	$Ni(qo)_2$	31
	Cu(II)	$Cu(qo)_2$	35
$pqoH^1$	Fe(III)	$Fe(qo)_3$	34
	Cu(II)	$Cu(qo)_2$	37
	Mn(II)	$Mn(qo)_2$	37
1-nqoH	Fe(III)	$Fe(qo)_3$	38
	Cu(II)	$Cu(qo)_2$	39
	Ni(II)	$Ni(qo)_2$	40
	Co(III)	$Co(qo)_3$	41

$pqoH^1$ =

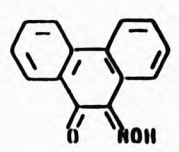
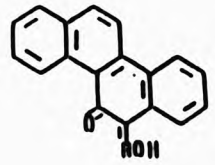


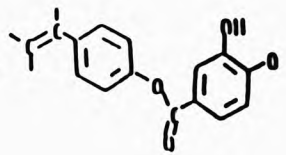
Table 1.1 continued

1,2 Quinone mono-oxime	Metal (ox. state)	Complex	Ref.
cqoH[2]	Cu(II)	$Cu(qo)_2$	37
	Mn(II)	$Mn(qo)_2$	37
	Ni(II)	$Ni(qo)_2$	37
vqoH[3]	Fe(II)	$Na[Fe(qo)_3]$	42,43,44,45
phqoH[4]	Ru(II)	$M[Ru(qo)_3]$	46
4-Bu^{t}qoH	Cu(II)	$Cu(qo)_2$	47
4-HSO_3qoH	Co(III)	$Co(qo)_3$	48

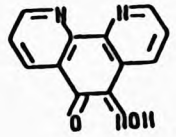
cqoH[2] =



vqoH[3] =



phqoH[4] =



The direct method involves the interaction of the 1,2-quinone mono-oxime with an appropriate metal salt (Reaction 1.5). This method is very old and has been applied extensively for the synthesis of several nickel(II), copper(II) and zinc(II) complexes. However, it has a limited applicability since only few 1,2-quinone mono-oximes are readily available.

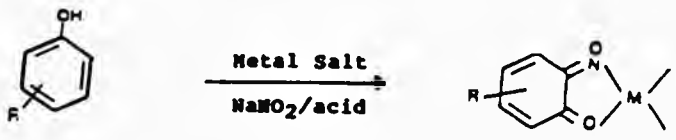
$$ML_n + n(qoH) \xrightarrow{H_2O,\ MeOH} M(qo)_n + nLH$$

L = Cl, SO_4

qoH = 1,2-quinone mono-oxime

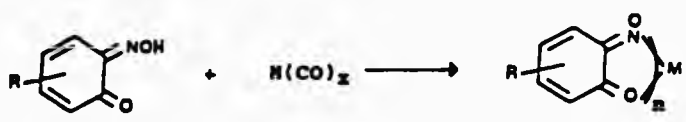
(Reaction 1.5)

The nitrosation method involves the nitrosation of a phenol using sodium nitrite and acetic acid in the presence of a transition metal salt.[49] The 1,2-quinone mono-oxime ligand is generated *in situ* and immediately forms a complex with the metal ion (Reaction 1.6). Complexation stabilises the anionic ligand by preventing it from undergoing further reactions. This method was first reported by Cronheim[8] and was later extended by other workers to prepare a number of complexes of type $M(qo)_n$ (M = V,[50] Fe,[38] Ni,[49] Cu,[49] Co[51], Mn[52]).



(Reaction 1.6)

The metal carbonyl method involves the interaction of a 1,2-quinone mono-oxime with a metal carbonyl (Reaction 1.7). So far, only the reactions of iron(0) pentacarbonyl[38] and dicobalt(0) octacarbonyl[41] with 1,2-naphthoquinone 1-oxime, 1,2-naphthoquinone 2-oxime, and 5-methoxy-1,2-benzoquinone 2-oxime have been reported.



(Reaction 1.7)

In the reactions involving iron(0) pentacarbonyl, it has been shown that the iron(II) complex is formed as the major product. In the case of dicobalt(0) octacarbonyl, cobalt(III) and cobalt(II) complexes are obtained.

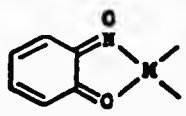
The ligand exchange method involves the reaction of the appropriate 1,2-quinone mono-oxime with a metal complex (e.g. Reaction 1.8).[60]

$$M(acac)_n + 1\text{-nqoH} \longrightarrow M(1\text{-nqo})_n + acacH$$

(Reaction 1.8)

1.2.5 Structure of 1,2-quinone mono-oxime complexes

Metal complexes of 1,2-quinone mono-oximes have been formulated with either a quinone oximic (1.11 and 1.12) or a nitrosophenolic structure (1.13 and 1.14). They have also been described as being a resonance hybrid of these two extremes. Structurally further complications arise from the possibility that the oximato (nitroso) group can potentially co-ordinate to the metal through the nitrogen and/or oxygen atom (1.15).



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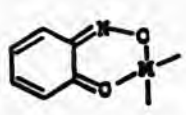

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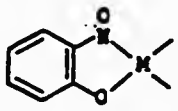

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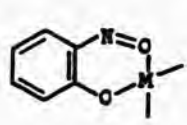

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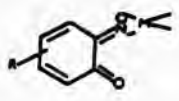


1.15

Several workers interpreted the infra-red spectra of the complexes of 1,2-naphthoquinone 1-oxime as indicating the presence of six-membered chelate ring involving co-ordination through the NO oxygen and CO oxygen atoms.[52] Furthermore, the structure of the ligand within these complexes is said by those authors to involve resonance contributions. The latter suggestion was based on studies of solution electronic spectra of the complexes and of their infra-red spectra in the solid state. In both cases the conclusions were drawn from comparisons of the spectra of the complexes with those of the free ligand. However, re-examination of the complexes by other workers showed that the six-membered ring structure is unlikely.[29,33] The latter authors carried out an infra-red spectroscopic study of quinone mono-oximes and of their complexes with copper(II), nickel(II) and iron(II). Their study resulted in the conclusion that the ligand is bound to the metal via the nitrogen atom of the NO group and the ring oxygen. This suggests a five-membered ring structure. They further concluded that the oximic contribution to the stucture is significant.

More recently, a number of X-ray crystallographic studies of quinone mono-oxime complexes have been

undertaken.[16,39,53-55] One such study was also completed during the course of this work and is presented in Chapter 3. These investigations showed that the most significant contribution is from the quinoneoximic structure. The X-ray studies have also established that, in most cases, the bonding of the NO group to the metal is through the nitrogen atom.

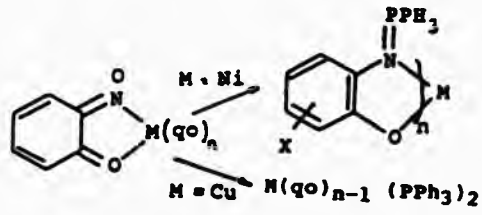
However, recent X-ray studies on some complexes involving heavier metals have shown a different type of bonding can occur.[32] In the complexes diaquobis (1,2-naphthoquinone 1-oximato) dioxouranium(VI) (triphenylphosphine oxide) and diaquobis(1,2-naphthoquinone-2-oximato) dioxouranium(VI)-trichloromethane dioxouranium (VI), the quinoneoximato ligand is bound to the metal through the nitrogen and the oxygen of the NO group. Bonding involving only the NO group has also been observed in platinum and gold complexes derived from 4-isonitroso-3(R)-isoxazol-5-one. However, in these complexes, bonding to the metal is only through the nitrogen atom of the NO group.[56]

1.2.6 Applications of metal complexes of 1,2-quinone mono-oximes

Many metal complexes of 1,2-quinone mono-oximes have been developed for analytical purposes and are still widely used in this context.[57] For example, in 'superalloys', cobalt may be selectively determined in the presence of nickel by the interaction of 1,2-naphthoquinone 1-oxime in alcohol with an aqueous

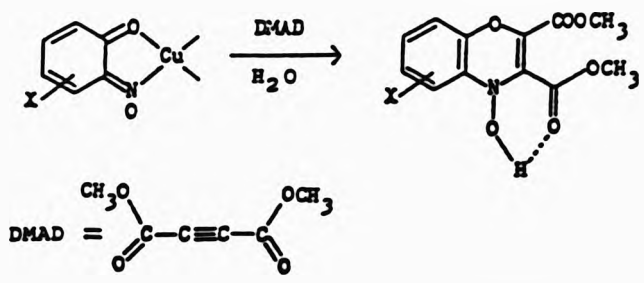
solution of the metal at low pH. The use of 1,2-naphthoquinone 1-oxime and its sulphonated derivatives for the analysis of iron and for the separation of impurities from iron-containing samples is well-documented. The ability of the 1,2-quinone mono-oximes to precipitate certain metals forms the basis for a number of separation techniques. For example, the precipitation of $Pd(1\text{-nqo})_2$ or $Co(1\text{-nqo})_3$ enables the metal to be quantitatively estimated. A number of the complexes have also found use in the paint, rubber and dye industries; for instance iron complexes of quinone mono-oximes have found considerable use as dye materials.[58] A dye based on a soluble derivative of an iron(II) trischelate has recently been patented and acts specifically on polyamide fibres.[59]

The present interest in complexes of quinone mono-oximes also reflects their importance in the synthesis of a wide variety of compounds. Various nickel(II) and zinc(II) complexes react with triphenylphosphine to give iminophosphorane complexes [60,61](Scheme 1.2). In the case of copper(II) complexes, reduction of the metal occurs, producing an adduct of the type $Cu(qo)(PPh_3)_2$ and dihydroxyphenazine.[62,63] Reduction of metal also occurs in the case of the $Fe(qo)_3$ complexes with the formation of an $Fe(qo)_2$ complex and of phenazine.[58]



(Scheme 1.2)

Other investigations have shown that the interaction of bis (1,2-quinone mono-oximato) copper (III) complexes with dimethylacetylenedicarboxylate provides a convenient route to 1,4-benzoxazines (Reaction 1.9).[64,65]



(Reaction 1.9)

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CHAPTER TWO

COMPLEXES OF RHODIUM AND IRIDIUM DERIVED FROM MONO OXIMES OF 1,2-NAPHTHOQUINONE

2.1 Introduction

As indicated in Table 1.2, the studies of metal complexes of 1,2-quinone mono-oximes have been concerned mainly with complexes of first row transition metals. Very little work has been reported on the formation and properties of complexes of second and third row transition metals. During the course of this study, X-ray crystallographic studies of actinide metal (e.g. uranium[1]) and second row transition metal (e.g. ruthenium[2]) complexes have been reported. The few other studies of second and third row transition metals reported in the literature have been concerned mainly with extraction and analytical aspects.[3-6] As a consequence, this chapter describes attempts to obtain complexes of rhodium(III) and iridium(III) of 1,2-naphthoquinone 1-oxime and 1,2-naphthoquinone 2-oxime.

Rhodium and iridium have extensive co-ordination chemistry. For both metals, all the oxidation states from (0) to (IV) are found. Compounds involving the metal in other oxidation states are also known. The most common oxidation state of both metals is (III). Neutral, anionic and cationic complexes have been reported for both metals. All iridium (III) complexes are kinetically inert, whereas most anionic complexes of rhodium (III) are relatively labile.

In contrast to cobalt(III) complexes, reduction of rhodium(III) or iridium(III) complexes does not give rise to divalent complexes. Thus depending on the nature of the ligand and on the conditions, reduction may lead to the metal or to hydridic species of M(III) or to M(I) when π-bonding ligands are involved. With few exceptions, phosphorus, arsenic and sulphur donors reduce iridium(IV) to iridium(III).

2.2 Complexes of rhodium and iridium

The synthesis and study of iridium(III) and rhodium(III) complexes have presented considerable problems. This is generally because the reactions involving the synthesis of these complexes are often slow and lead to mixtures of products and/or isomers.

Many anionic complexes of rhodium and iridium have been reported. The complexes which have attracted much attention are those derived from oxalate ions. A number of such complexes have been reported[7-19] but until recently these have only been obtained in poor yields. For instance, several workers carried out the preparation of potassium tris(oxalato)iridate(III) by heating an aqueous solution of potassium hexachloroiridate(III) and potassium oxalate in a sealed tube at 130 ^{o}C.[15] The reaction is slow and gives the desired product in 30% yield. The low yield has been attributed to the difficulty in separating the product from excess potassium oxalate. Recently, Flynn & Demas successfully

resolved the products by applying a novel extraction step in their procedure.[16] This involved the addition of a tetraalkylammonium salt, for example, tetrabutylammonium hydrogen sulphate or tetrabutylammonium chloride to precipitate tetraalkylammonium tri(oxalato)iridate(III) which was extracted with nitromethane. Their method is regarded as simpler than the sealed tube method and gives yields of up to 80-85%. Similar yields are obtained when potassium hexabromoiridate (IV) is used. Significantly the reaction was complete within 24 hours compared to the several days required when hexachloroiridate(III) is used and gives equally good yields of potassium tris(oxalato)iridate(III). With iridium dioxide, oxalic acid gives polynuclear complexes of ill-defined composition.

Alkali salts of the tris(oxalato) anion $[Rh(C_2O_4)_3]^{3-}$ have also been reported.[8,17,18] However, the reactions have not been found to be reproducible and show conflicting results. The reaction between $RhCl_3$ and oxalic acid has been shown to give $[Rh(C_2O_4)_3]^{3-}$.[9] However, the reaction is incomplete and other aquo-co-ordinated oxalato complexes of rhodium are formed in smaller amounts. There is evidence that in order to obtain complete conversion of rhodium(III) to $K_3[Rh(C_2O_4)_3]$, the chloride must be refluxed with 4-5 times its weight of potassium oxalate for at least seven hours.

The study of neutral complexes of rhodium and iridium derived from anionic bidendate ligands has received very

little attention. The complexes which have received extensive studies are derived mainly from β-diketones. Some examples are shown in Table 2.1.

The preparation of such complexes appears to be even more complicated than that of the anionic or cationic complexes.

The first attempts to synthesise the tris-chelate of acetylacetone using rhodium hydroxide or sodium chlorhodate(III) were unsuccessful.[20] The compound was obtained, and then only in low yield, when sodium hexachlorohodate(III) was refluxed with sodium acetylacetonate. Better results were obtained by heating a mixture of rhodium nitrate with acetylacetone at pH 4. Similarly, the iridium complex was obtained but again only in small yield, from iridium(III) hydroxide and acetylacetone. Attempts to prepare it from iridium dioxide were unsuccessful.

2.3 Preparation of rhodium and iridium complexes of 1,2-naphthoquinone mono-oximes

In this chapter the results of a systematic study, undertaken as part of the work for this thesis, on the synthesis and characterisation of several complexes of 1,2-naphthoquinone 1-oxime and 1,2-naphthoquinone 2-oxime are presented.

Table 2.1 Some reported complexes of rhodium and iridium

Reactants		Method of preparation	Formula proposed	Ref.
Metal salt	Ligand			
$RhCl_3\ 3H_2O$	hfacH	a, b, c	$Rh(hfac)_3$[g], $RhCl(hfac)_2$[f]	20, 21
$Rh(NO_3)_3$	hfacH	c	$Rh(hfac)_3$[g]	21
$IrO_3\ 3H_2O$	acacH	c, d	$Ir(acac)_3$[g]	22
$Ir(OH)_3$	acacH	c	$Ir(acac)_3$[h], $H[Ir(OH)_2(acac)_2]$[h]	22
$Na_3[IrCl_6]$	en	c	$[Ir(en)_3]Cl_3$[g]	23
Rh_2O_3	acacH	c	$Rh(acac)_3$[h]	22
$Rh(NO_3)_3$	acacH	c, e	$Rh(acac)_3$	22
$Na[RhCl_6]$	en	c	$[Rh(en_3)]Cl_3$	24, 25

a = in basic aqueous solution; b = in absolute ethanol; c = aerobic conditions: d = pH 6; e = pH 4;

f = dimer; g = mixture of optical isomers or cis- and trans- isomers;

h = low yield.

hfacH = hexafluoroacetylacetone
acacH = acetylacetone
en = ethylenediamine

The following synthetic methods were investigated:

1 The direct reaction of 1,2-naphthoquinone 1-oxime, 1,2-naphthoquinone 2-oxime or sodium 1,2-naphthoquinone 1-oximate with hydrated rhodium(III) chloride or chloroiridic(III) acid.

2 The nitrosation of 2-naphthol or 1-naphthol in the presence of hydrated rhodium(III) chloride or chloroiridic(III) acid.

2.3.1 The reaction of 1,2-naphthoquinone 1-oxime or potassium 1,2-naphthoquinone 1-oximate with rhodium(III) chloride hydrate

The direct interaction between 1,2-naphthoquinone 1-oxime and hydrated rhodium(III) chloride was investigated under various conditions. Table 2.2 indicates the results of these reactions.

When 1,2-naphthoquinone 1-oxime in methanol was reacted with hydrated rhodium(III) chloride a complex mixture was obtained. Filtration of the mixture gave a reddish-brown solid. T.l.c. examination of the solid showed it to consist of several products. Attempts to resolve the mixture into its components by silica-gel column chromatography using toluene, chloroform, ethyl acetate and mixtures of these solvents proved unsuccessful. Attempts to separate the products by recrystallisation from toluene, chloroform, ethyl acetate, acetone, dichloromethane and mixtures of these solvents were also unsuccessful.

Table 2.2 Reaction between 1,2-naphthoquinone 1-oxime and hydrated rhodium(III) chloride

Solvent	Reaction Time (h)	Reactants		Products	
		$RhCl_3.3H_2O$ (mol.equiv.)	1-nqoH (mol. equiv.)	Solid B Rh(1-nqo)$_3$[a] (% yield)[3]	Solid C
Methanol	72	1	3	41	Rh(1-nqo)$_3$[a] and several other products[b]
Aq. methanol	1	1	3	36	Rh(1-nqo)$_3$[a] and several other products[b]
Methanol	48	1	3	48	Rh(1-nqo)$_3$[a] and several other products[b]
Acetic acid	24	1	3	56	Rh(1-nqo)$_3$[a] and several other products[b]
Acetic acid	36	1	3	63	Rh(1-nqo)$_3$[a] and several other products[b]

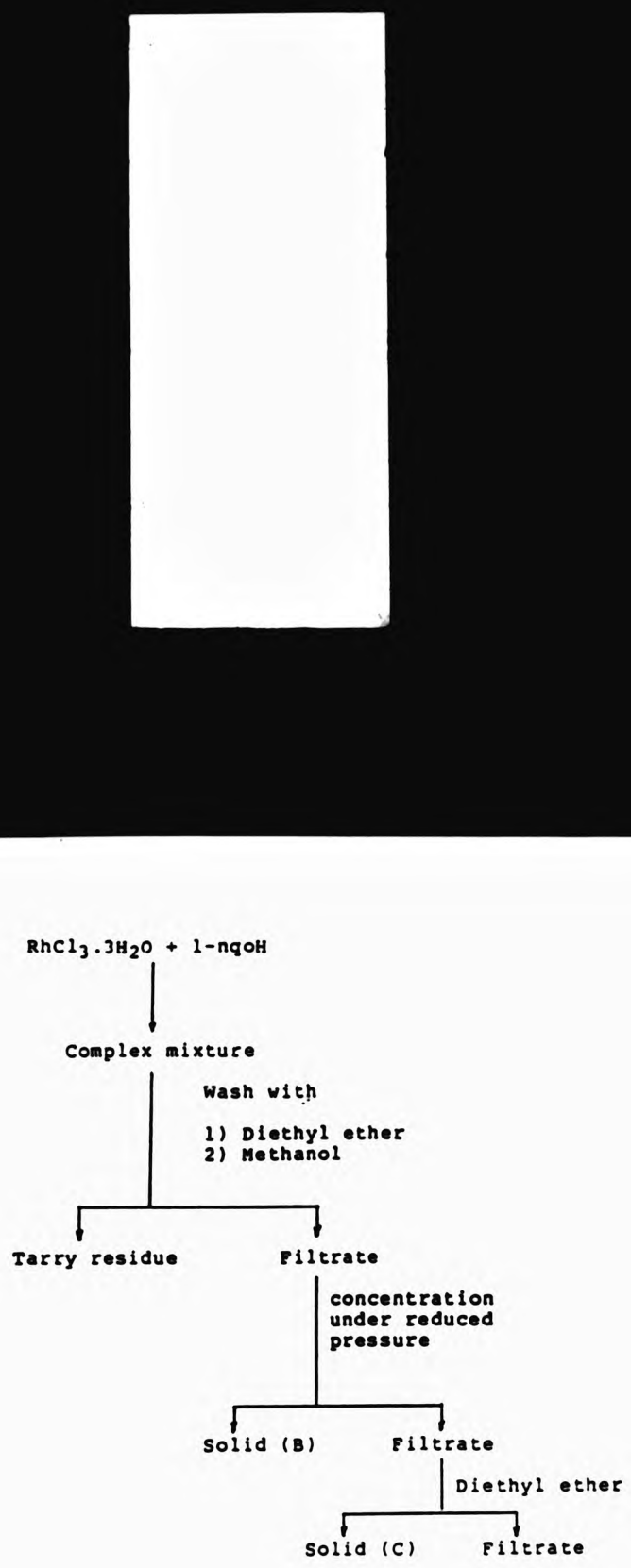
a = mixture of two isomers.
b = as indicated by t.l.c.

Some separation, however, was achieved by a combination of extraction and precipitation techniques. Scheme 2.1 outlines the approach used. Extraction of the solid obtained from the reaction with ether and methanol afforded a small amount of a tarry residue and an orange extract. The extract on concentration gave the main product, a red crystalline solid (Solid B) which was separated by filtration. Addition of ether to the filtrate gave a small amount of another solid (Solid C).

T.l.c. indicated the presence of two components in Solid B. However, elemental analysis was in excellent agreement with the formulation $Rh(C_{10}H_6NO_2)_3$ suggesting that the two components must be due to the presence of isomers. The i.r. showed bands in the region of 1500-1620cm^{-1} characteristic of the chelated quinoneoximato anion. Further support for the formulation Rh(1-nqo)$_3$ is provided by its diamagnetic character which is indicative of low spin rhodium(III). Attempts to resolve the two isomers by column and preparative t.l.c. (silica gel) were unsuccessful.

In the case of Solid C, t.l.c. indicated the presence of two isomers of Rh(1-nqo)$_3$ as well as of at least two other components. Attempts to separate the components were unsuccessful.

The formation of isomers is not entirely unexpected when one considers that for a complex involving the chelated naphthoquinone oximato anion, linkage isomers are possible as a result of the ambidentate nature of the ligand (cf. Figures 2.1 and 2.2).



Scheme 2.1 Schematic representation of separation technique used for the products arising from the reaction between $RhCl_3.3H_2O$ and 1-nqoH.

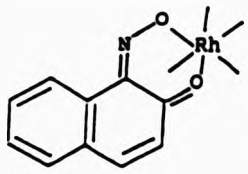


Figure 2.1

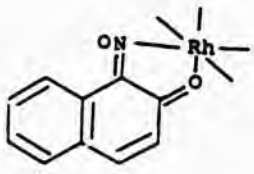


Figure 2.2

Furthermore, facial and meridial isomers are possible because of the asymmetric character of the ligand (Figures 2.3 and 2.4). In the case of $Co(1\text{-nqo})_3$ such isomers have been detected by n.m.r.[26] Also in the case of tris(1,1-trifluoro-2,4-pentanedionato)cobalt(III), facial and meridial are known to exist (Figures 2.5 and 2.6).[27]

facial

Figure 2.3

meridial

Figure 2.4

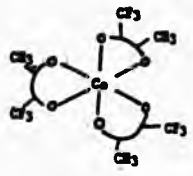


Figure 2.5

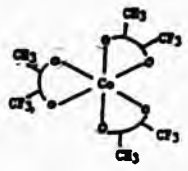


Figure 2.6

A mixture of isomers were also formed when 1,2-naphthoquinone 1-oxime and hydrated rhodium(III) chloride were mixed in different solvents (Table 2.2). From t.l.c. examinations the mixtures were identical. However, none of the complexes could be isolated in appreciable yields. The yield of the $Rh(1\text{-nqo})_3$ improved when the reaction was carried out in an acidic medium.

When the reaction of rhodium(III) chloride hydrate with 1,2-naphthoquinone 1-oxime was carried out in acetic acid/acetate buffer solutions at between pH 5-6 the yield of the complex $Rh(1\text{-nqo})_3$ was quantitative. The reaction gave a less complex mixture and separation was readily achieved. The reaction of Na(1-nqo) with hydrated rhodium(III) chloride also afforded the rhodium tris-chelates in satisfactory yield.

2.3.2 Reaction of 1,2-naphthoquinone 2-oxime with hydrated rhodium(III) chloride

As in the case of 1,2-naphthoquinone 1-oxime, when 1,2-naphthoquinone 2-oxime was reacted with rhodium(III) chloride in methanol a complex mixture resulted. Filtration of the mixture gave a purple solid which was found to be multicomponent by t.l.c. examination. The main component of the mixture, a purple solid, was again separated by using a combination of extraction and chromatographic techniques.

The elemental composition of the purple solid corresponds to a 1:3 rhodium:ligand ratio, and is indicative of the formulation of $Rh(2\text{-nqo})_3$. The solid

was found to be diamagnetic, in line with the oxidation state (III) for rhodium. T.l.c. showed, as in the case of $Rh(1\text{-nqo})_3$, the presence of two components, thus indicating that the complex is a mixture of isomers.

The complex $Rh(2\text{-nqo})_3$ was also obtained but in higher yield, from the interaction of rhodium(III) chloride with 1,2-naphthoquinone 2-oxime in acetic acid/acetate buffer solution at pH5-6. The reaction of potassium 1,2-naphthoquinone 2-oxime with hydrated rhodium(III) chloride also afforded the rhodium tris-chelates in high yield. In contrast, in the absence of a buffer the latter reaction gave the complex in poor yield.

2.3.3 The reactions between 1,2-naphthoquinone 1-oxime, sodium-1,2-naphthoquinone 1-oxime or 1,2-naphthoquinone 2-oxime and hydrated chloroiridate $[IrCl_6]^{3-}$

The reactions between 1,2-naphthoquinone 1-oxime or sodium-1,2-naphthoquinone 1-oxime with hexachloro-iridic(III) acid, obtained by the reduction of chloroiridic(IV) acid, were carried out under various conditions. Table 2.3 summarises the results.

When methanol was used as the solvent, no reaction occurred at room temperature but after prolonged reflux a mixture of products resulted. Attempts to resolve the mixture using column chromatography proved unsuccessful. Recrystallisation from toluene, chloroform and acetone was also unsuccessful. However, treatment of the mixture with excess pyridine afforded a brown solid in low yield,

Table 2.3 Reaction between 1,2-naphthoquinone 1-oxime and chloroiridic acid solution[a]

Solvent	Reactants		Reaction		Products
	Ir(III) (mol.equiv.)	1-nqoH (mol. equiv.)	Time(d)	Temp	
Methanol	1	3	10	20	No reaction
Methanol	1	3	5	R	Mixture[cb]
Aq. Methanol	1	3	6	R	Mixture[c]
Acetic acid/Methanol	1	3	5	R	Mixture[c]
Acetic acid	1	3	5	R	Mixture[c]

a = Obtained by the reduction of chloroiridic(IV) acid with propan-2-ol at 80°C.
b = As indicated by t.l.c.
c = Reaction with pyridine afforded [pyH][Ir(1-nqo)Cl_3py] (cf. Chapter 3).

whose formulation was established as [pyH][Ir(1-nqo)Cl_3py] (Figure 2.7) using X-ray crystallography (see Chapter 3). Similar results were obtained when the reaction between 1,2-naphthoquinone 1-oxime and chloroiridic(III) acid was carried out in aqueous methanol, aqueous acetic acid and acetic acid.

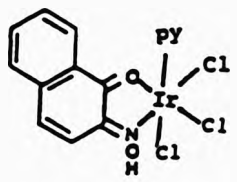


Figure 2.7

Reaction of chloroiridic(III) acid with excess sodium 1,2-naphthoquinone 1-oximate in the presence of a buffer (pH 4-5), again afforded a mixture of products. This mixture on chromatography gave a brown solid which contained two components with similar Rf's.

The elemental analysis of this solid indicated the formulation of $Ir(1\text{-nqo})_3$, suggesting that, as in the case of $Rh(nqo)_3$, the two components in the solid correspond to isomers.

Analogous reactions involving 1,2-naphthoquinone 2-oxime and chloroiridic(III) acid also gave complex mixtures. From the mixture obtained from sodium 1,2-naphthoquinone 2-oximate in the presence of a buffer, a solid of composition $Ir(2\text{-nqo})_3$ could be isolated in very

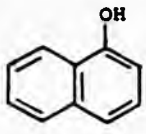
low yield, as a mixture of two isomers, using chromatography.

2.4 The nitrosation of 1-naphthol or 2-naphthol in the presence of hydrated rhodium(III) or choloroiridic acid solution

The nitrosation of 1-naphthol or 2-naphthol using sodium nitrite and acetic acid, in the presence of transition metal salts, has been used extensively for the preparation of transition metal complexes of 1,2-naphthoquinone 2-oxime and 1,2-naphthoquinone 1-oxime respectively. However, apart from the synthesis of ruthenium complexes of these compounds,[29] this approach has been used for the synthesis of only first row transition metal complexes.

In most cases the above reactions lead to neutral complexes of the type $M(nqo)_x$ (x = 2 or 3, nqoH = 1,2-naphthoquinone 2-oxime or 1,2-naphthoquinone 1-oxime). However, in some cases, anionic complexes are obtained together with the neutral complexes. For example, complexes of the type $Na[Co(nqo)_2(NO_2)_2]$ have been obtained in addition to neutral complexes of the type $Co(nqo)_3$, when the naphthols were nitrosated in the presence of cobalt(II) chloride.

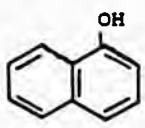
In the reactions involving cobalt(II) salts, oxidation of the metal occurs (e.g. Reaction 2.1).



$$\xrightarrow[CoCl_2]{NaNO_2/acid} Co(2\text{-nqo})_3 + Na[Co(2\text{-nqo})_2(NO_2)_2]$$

Reaction 2.1

In contrast, when the naphthols are nitrosated in the presence of iron(III) salts, reduction of the metal occurs, to some extent, and mixtures of iron(II) and iron(III) result (Reaction 2.2).



$$\xrightarrow[FeCl_3]{NaNO_2/acid} Fe(2\text{-nqo})_2 + Fe(2\text{-nqo})_3$$

Reaction 2.2

In this study, the nitrosation of 1-naphthol or 2-naphthol in the presence of hydrated rhodium(III) chloride or chloroiridic(III) acid was carried out with the aim of providing an alternative approach to the preparation of rhodium or iridium complexes derived from 1,2-naphthoquinone mono-oximes.

2.4.1 The nitrosation of 1-naphthol or 2-naphthol in the presence of rhodium(III) chloride

Nitrosation of 2-naphthol using sodium nitrite in the presence of hydrate rhodium(III) chloride in acetate buffer gave a red solid. T.l.c. examination showed this solid to be a mixture of $Rh(1\text{-nqo})_3$ and several other minor products.

The separation of this mixture on a silica gel column using toluene followed by ethyl acetate and acetone as eluant proved only partially successful. However, separation of the $Rh(1\text{-nqo})_3$ complex was conveniently achieved by solvent extraction. The mixture was extracted using a Soxhlet apparatus with ether and chloroform. The ether extract yielded mainly organic components and pure $Rh(1\text{-nqo})_3$ was obtained in good yield from the chloroform extract. Similarly, 1-naphthol afforded $Rh(2\text{-nqo})_3$ which was purified in an analogous fashion.

Significantly, in both cases no change in the oxidation state of the metal occurred.

2.4.2 The nitrosation of 1-naphthol or 2-naphthol in the presence of chloroiridic(III) acid

In contrast to the behaviour of the naphthols in the presence of rhodium(III) chloride, the nitrosation in the presence of chloroiridic(III) acid did not lead to complexes of iridium. In both cases, the reaction afforded the respective naphthoquinone mono-oxime. This behaviour is in accord with the observation that

chloroiridic(III) acid reacts only to a small extent and under vigorous conditions with naphthoquinone mono-oximes.

2.5 Reaction of $M(nqo)_3$ with Lewis bases

The quinoneoximic complexes are multifunctional compounds and can undergo a variety of reactions with e.g. Lewis bases, deoxygenating agents and dienophiles. The behaviour of the metal complexes towards Lewis bases has been the subject of an increasing amount of attention in recent years.[31-37]

Transition metal chelates undergo three main types of reaction with Lewis bases. These are, i) adduct formation, ii) ligand modification, or iii) internal redox reaction. The nature of the reaction between metal chelates and Lewis bases has been shown to be affected by a number of factors which include the type of Lewis base, the chelating ligand, the metal and the solvent employed.

Studies of the reactions between 2nd and 3rd row transition metal 1,2-naphthoquinone mono-oximic complexes and Lewis bases are limited to that of the bis chelates of ruthenium(II). In these cases the reaction leads to adduct formation of the type $Ru(nqo)_2(LB)_2$ (LB = pyridine or triphenyl-phosphine).[28]

Analogous reactions involving rhodium and iridium complexes have not been carried out previously. In view of the well-known ability of rhodium and iridium to exhibit several oxidation states, the interaction of

rhodium(III) or iridium(III) quinoneoximates with Lewis bases was undertaken.

2.5.1 Interaction of $Rh(nqo)_3$ and $Ir(nqo)_3$ with Lewis base

The $Rh(nqo)_3$ complexes showed no tendency to react with pyridine, under reflux conditions as indicated by t.l.c. and quantitative recovery of the reactants. This is in marked contrast to the behaviour of other transition metal complexes of the naphthoquinoneoximes which often afford adducts (e.g. Reaction 2.3) or undergo complex internal redox reaction (e.g. Reactions 2.4 and 2.5).[30,37]

$$Cu(nqo)_2 + py \longrightarrow Cu(nqo)_2(py)$$

Reaction 2.3

$$Fe(1\text{-}nqo)_3 + py \longrightarrow Fe(1\text{-}nqo)_2(py)_2 + [1\text{-}nqo^{\cdot}]$$

$[1\text{-}nqo^{\cdot}]$ $\xrightarrow{\text{Abstraction of } H^{\cdot} \text{ from solvent}}$ 1-nqoH

Reaction 2.4

$$Mn(nqo)_3 + py \xrightarrow{air} [Mn(nqo)_2O] + [nqo^{\bullet}] \downarrow \text{other products}$$

Reaction 2.5

Tris(1,2-naphthoquinone-2-oximato) rhodium(III) also failed to react with triphenylphosphine even under prolonged reflux conditions. Again this contrasted the behaviour of other analogous transition metal complexes derived from 1,2-quinone mono-oximes which show either deoxygenation behaviour (e.g. Reaction 2.6)[34] or internal redox behaviour (e.g. Reaction 2.7) with the phosphine.[30]

Reaction 2.6

Reaction 2.7

As in the case of the rhodium complexes, neither $Ir(1\text{-}nqo)_3$ or $Ir(2\text{-}nqo)_3$ reacted with pyridine or triphenylphosphine.

This contrasting behaviour is not entirely unexpected when the crystal field stabilisation energies (CFSE) are

considered. Since all other factors are more or less equal (e.g. iron(III), cobalt (III), rhodium(III) and iridium (III) trischelates involve identical ligands and have similar geometries (Figure 2.8), the difference in their stabilities can be ascribed to their CFSE.

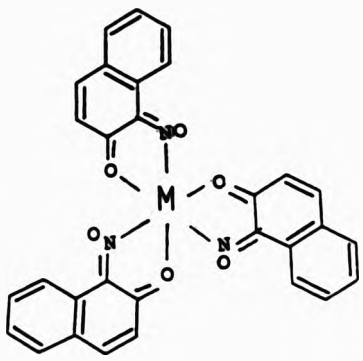


Figure 2.8

Since the crystal field stabilisation energy of spin paired d^6 electronic configuration is greater than the corresponding d^7 configuration it can be seen that the oxidation state(III) of cobalt(III) or iridium(III) is preferred to the cobalt(II), rhodium(II) or iridium(II). This contrasts markedly with the corresponding iron complexes where the d^6 configuration is more stable than the d^5 configuration, resulting in the oxidation state (II) of iron being more favourable than the oxidation state (III). This can be seen in their CFSE, the iron(III) octahedral complex has a CFSE of -10/5 compared

to -12/5 for its iron(II) (e.g. the bispyridine adduct of iron(II) bischelate) octahedral complex suggesting the reduction to the (II) state is preferred. In contrast, the cobalt(III), rhodium(III) or iridium(III) octahedral complexes has a value of -12/5 compared with -9/5 for a postulated cobalt(II), rhodium(II) or iridium(II) octahedral complex. This suggest that reduction is not favourable in the rhodium or iridium system but strongly so in the corresponding iron system.

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CHAPTER THREE

CRYSTAL STRUCTURE OF PYRIDINIUM TRICHLORO (1,2-NAPHTHOQUINONE 1-OXIMATO)(PYRIDINE) IRIDATE(III)

3.1 The crystal structure of [pyH][Ir(1-nqo)Cl_3py]

Crystal data: Ir($C_{10}H_{17}IrN_3O_2Cl_3$) M = 630.5

The crystal was shown to be monoclinic. The space group, from systematic absences is $P2_1/c$ with a = 11.403(3); b = 11.977(4) Å; c = 15.155(5) Å; U = 2062.87 Å; Z = 4, D_c = 1.810 g cm^{-3} f(000) = 1660, MoK radiation. (λ = 0.71069 A) μ(Mo - K_α) = 67.55 cm^{-1}.

3.2 Determination of the structure

A Phillips PW1100 computer controlled four-circle, single crystal diffractometer with θ - 2θ scan was used for data collection. Reflection with $3.0 < \theta < 25.0^\circ$ were examined. A constant scan speed of 0.05 s^{-1} and scan width of 0.8° were used, with a background measuring time equal to half the scan time. Three standard reflections were examined every three hours during data collection and showed no significant variation in intensity. The intensities were calculated from the peak and background measurements with a programme written for the PW1100 diffractometer[1]. The variance of the intensity I was calculated as $[\{\sigma_c(I)\}^2 + (0.04I)^2]^{\frac{1}{2}}$ where $\{\sigma_c(I)\}^2$ is the variance due to counting statistics and the term $(I)^2$ was introduced to allow for other sources of error. I and $\sigma(I)$ were corrected for Lorentz polarisation factors. Absorption corrections were applied using 340 azimuthal scan data and relative transmission factors ranged from 1.00 to 340. The final data consisted of 2884 independent reflections of which

2816 were considered to be observed with $I > 3\sigma(I)$ and used in the refinement.

The following systematic absences were observed in the data:

0k0	**absent unless**	**k = 2n**
h0l	**absent unless**	**h + l = 2n**

This showed the space grouping to be $P2_1/c$. The unit cell dimensions were calculated by a programme of the diffractometer utilising the measured angles of 25 reflections at θ approximately 10°.

The number of molecules in the unit cell was assumed to be 4 since the density for the compound was calculated to be 1.83 g cm^{-1}. A Patterson vector map was calculated and searched for vector peaks due to symmetry related iridium atoms. The space group indicated that there would be three such peaks having Patterson u, v, w co-ordinates related to the atomic x, y, z co-ordinates of the iridium atom in the real cell as follows:

u	v	w	
0	$\frac{1}{2}-2y$	$\frac{1}{2}$	(1)
$-2x$	$-\frac{1}{2}$	$\frac{1}{2}-2z$	(2)
$2x$	$2y$	$2z$	(3)

A peak corresponding to (1) was found at u, v, w values of 0.00, 0.354, 0.50; its peak intensity was 458. From

this y was calculated to be 0.073. The peak corresponding to 2 was found at u, v, w values of -0.484, 0.500, -0.069; its peak intensity was 415. From this, x was calculated to be 0.242 and z as 0.2155. Using these results the peak corresponding to the 2x, 2y, 2z vector was found at u, v, w values of 0.484, 0.146, 0.569; its peak intensity was 203.

Least square refinement of the Patterson co-ordinates of the iridium atom located from the Patterson synthesis gave an R-factor of 0.35. From the first electron density map produced from a Fourier difference synthesis the position of all atoms except the hydrogens were located. After subsequent least squares refinement of the atomic co-ordinate and isotropic thermal parameters, the R-value of 0.14 resulted. It was decided that for subsequent structure refinement anisotropic thermal parameters should be used for the heteroatoms (Ir, N, O, Cl) and refinement converged to R = 0.0366. All the hydrogen atoms for the compound were found from a subsequent difference map and included in the calculation of the structure factors but were not refined. The final R-factor for 262 parameters was 0.0364 and R_w = 0.0372 with $w = 1/\sigma^2 (F_o)$. The final difference map showed maximum of ca. 1 e $Å^{-3}$ approximately 1 Å for the iridium atom. Neutral atom scattering factors were used throughout and calculations were done using SHELX programmes.[2]

List of structure factor, rigid group positional, thermal parameter, bond lengths, bond angles are given in the following Tables:

Table 3.1 Fractional atomic co-ordinates and thermal parameter (Å).

Table 3.2 Fractional atomic co-ordinates for the hydrogen atoms.

Table 3.3 Anisotropic thermal parameter (Å).

Table 3.4 Bond lengths.

Table 3.5 Bond angles.

Table 3.6 Intermolecular distances.

Table 3.7 Intramolecular distances.

3.3 Discussion

Perspective view of the iridium complex, together with the atomic numbering and its unit cell, is shown in Figure 3.1 and Figure 3.2. Some bond lengths and bond angles are given in Figure 3.3 and Figure 3.4. In the discussion, the bond lengths are given to two significant figures to allow comparison with other reported data.

The iridium(III) atom adopts an octahedral co-ordination geometry. This is not surprising since all iridium(III) complexes are known to be octahedral. The X-ray crystal structure of the anhydrous ammonium salt $[NH_4]_3[IrCl_6]$ shows this to be cubic (a = 9.87 Å) and the complex anion is octahedral with iridium-chlorine distance of 2.47 Å.[3] The metal atom in $IrCl_3$ is also at the centre of a distorted octahedron of chlorine atoms, with three pairs of chlorine atoms, at 2.30, 2.31 and 2.39 Å in the α-form[4] and at 2.31(0), 2.33(6) and 2.41(0) in the β-form.[5] It is asserted that the difference between the two forms lies in the distribution of iridium atoms in the octahedral holes of the lattice. The

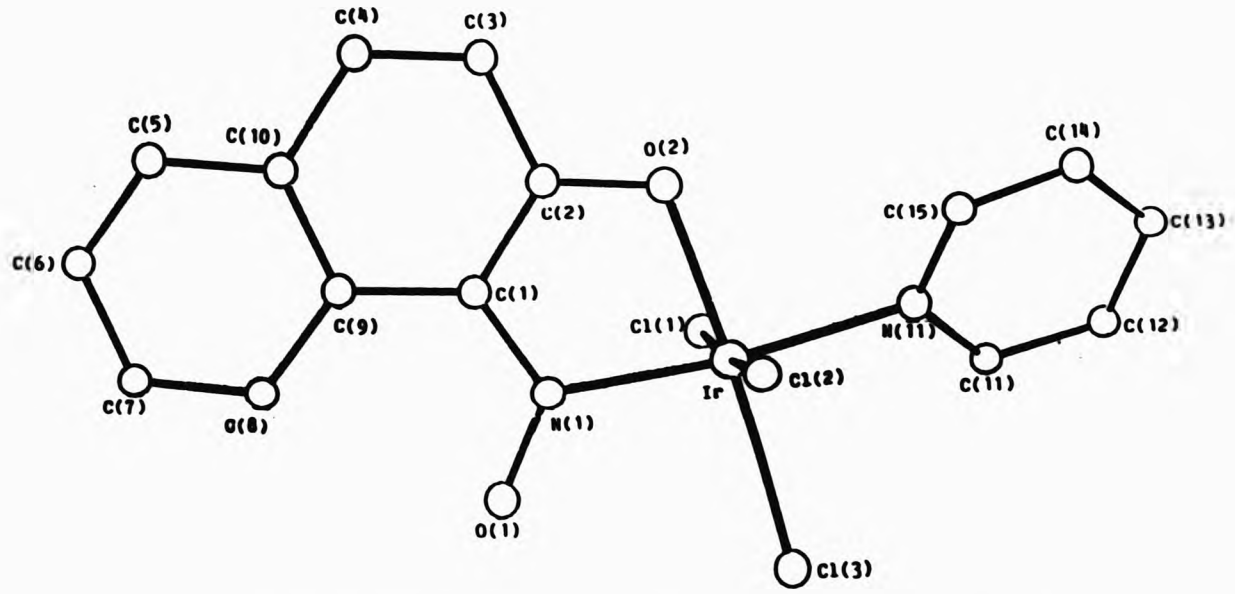


Figure 3.1 Structure of anion of $[pyH][Ir(C_{10}H_6NO_2)pyCl_3]$

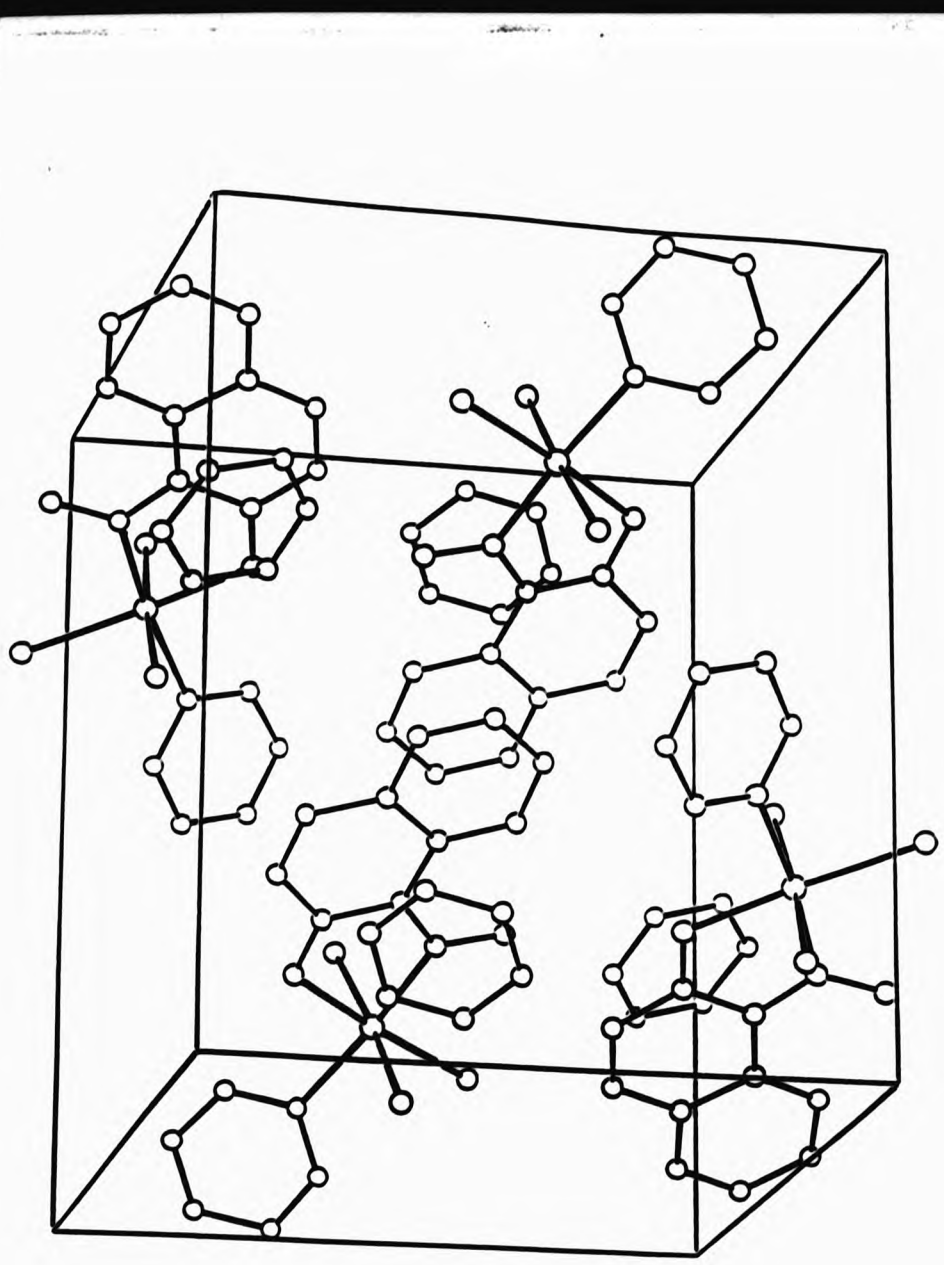


Figure 3.2 Unit Cell of [pyH][Ir($C_{10}H_6NO_2$)(py)Cl_3]

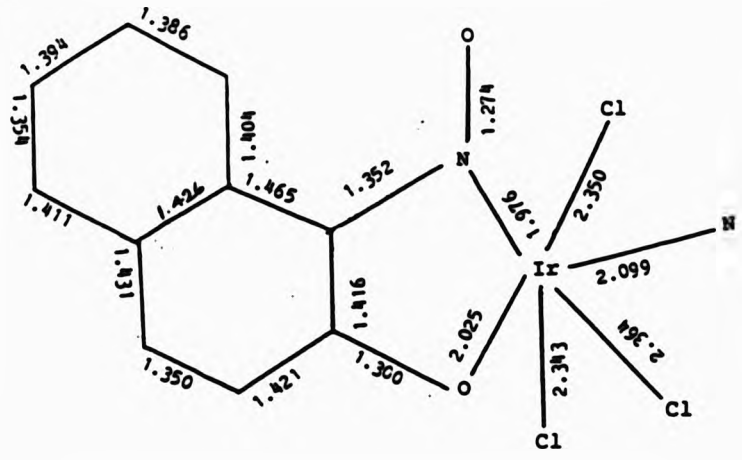


Figure 3.3 Bond lengths

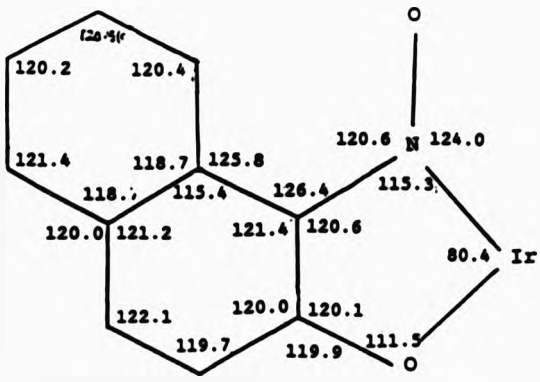


Figure 3.4 Bond angles

TABLE 3.1 Fractional atomic coordinates and thermal parameters ($Å^2$) for [pyH][Ir($C_{10}H_6NO_2$)pyCl_3]

Atom	x	y	z	U_{iso} or U_{eq}
Ir	0.24375(3)	0.07298(2)	0.28515(2)	0.0289(2)
Cl(1)	0.3829(2)	0.0620(2)	0.4074(1)	0.048(1)
Cl(2)	0.1058(2)	0.0982(2)	0.1629(1)	0.042(1)
Cl(3)	0.1539(2)	-0.0962(2)	0.3235(1)	0.043(1)
O(2)	0.3244(5)	0.2130(4)	0.2459(3)	0.037(3)
O(1)	0.3617(5)	-0.0987(4)	0.1918(4)	0.047(4)
N(1)	0.3573(5)	0.0052(5)	0.2092(4)	0.033(4)
N(11)	0.1326(5)	0.1613(5)	0.3641(4)	0.033(4)
C(1)	0.4347(7)	0.0770(6)	0.1769(5)	0.032(4)
C(2)	0.4099(7)	0.1895(6)	0.1973(5)	0.035(4)
C(3)	0.4761(7)	0.2772(7)	0.1622(5)	0.043(5)
C(4)	0.5640(7)	0.2526(7)	0.1110(6)	0.044(5)
C(5)	0.6929(8)	0.1184(8)	0.0828(6)	0.052(6)
C(6)	0.7266(8)	0.0127(10)	0.0254(6)	0.059(6)
C(7)	0.6669(8)	-0.0778(8)	0.0583(6)	0.052(6)
C(8)	0.5713(7)	-0.0609(7)	0.1077(5)	0.041(5)
C(9)	0.5331(7)	0.0477(6)	0.1250(5)	0.034(4)
C(10)	0.5966(7)	0.1399(7)	0.0930(5)	0.040(5)
C(11)	0.1037(8)	0.1187(8)	0.4420(5)	0.047(5)
C(12)	0.0327(8)	0.1775(9)	0.4947(6)	0.057(6)
C(13)	-0.0076(7)	0.2839(9)	0.4665(6)	0.055(6)
C(14)	0.0230(8)	0.3249(8)	0.3874(6)	0.056(6)
C(15)	0.0914(8)	0.2622(7)	0.3378(6)	0.046(5)
N(20)	0.2516(6)	-0.1997(6)	0.7065(4)	0.044(4)
C(20)	0.3245(7)	-0.1553(8)	0.6499(6)	0.048(5)

TABLE 3.1 continued

C(21)	0.3117(9)	-0.0468(8)	0.6255(7)	0.056(6)
C(22)	0.2242(8)	0.0169(8)	0.6582(7)	0.053(6)
C(23)	0.1502(8)	-0.0316(8)	0.7137(7)	0.056(6)
C(24)	0.1660(7)	-0.1405(8)	0.7385(6)	0.046(5)

TABLE 3.2 Fractional atomic coordinates for the hydrogen atoms for [pyH][Ir($C_{10}H_6NO_2$)pyCl_3]

Atom	x	y	z
H(24)	0.1095	-0.1778	0.7842
H(3)	0.4287	0.3583	0.1748
H(4)	0.6246	0.3094	0.0763
H(5)	0.7444	0.1983	0.0374
H(6)	0.8038	-0.0013	-0.0113
H(7)	0.6828	-0.1470	0.0406
H(8)	0.5315	-0.1341	0.1212
H(11)	0.1134	0.0259	0.4545
H(12)	0.0026	0.1503	0.5561
H(13)	-0.0681	0.3166	0.5104
H(14)	-0.0202	0.4152	0.3767
H(15)	0.1170	0.3050	0.2798
H(20)	0.3996	-0.1882	0.6407
H(20n)	0.2644	-0.2806	0.7251
H(21)	0.3558	0.0021	0.5885
H(22)	0.2060	0.1083	0.6278
H(23)	0.0884	0.0121	0.7564

TABLE 3.3 Anisotropic thermal parameters ($Å^2$) for [pyH][Ir($C_{10}H_6NO_2$)pyCl_3]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir	0.0337(2)	0.0240(2)	0.0292(2)	0.0012(1)	0.0178(1)	0.0025(1)
Cl(1)	0.044(1)	0.057(1)	0.043(1)	0.001(1)	0.008(1)	0.006(1)
Cl(2)	0.047(1)	0.045(1)	0.034(1)	0.001(1)	0.012(1)	0.005(1)
Cl(3)	0.051(1)	0.030(1)	0.048(1)	0.003(1)	0.030(1)	-0.002(1)
O(2)	0.042(3)	0.025(3)	0.044(3)	-0.000(3)	0.018(3)	-0.002(2)
O(1)	0.060(4)	0.022(4)	0.059(4)	-0.005(3)	0.037(3)	0.002(3)
N(1)	0.038(4)	0.032(4)	0.031(3)	0.003(3)	0.019(3)	-0.005(3)
N(11)	0.039(4)	0.031(4)	0.031(3)	-0.001(3)	0.015(3)	0.001(3)
C(1)	0.042(4)	0.024(4)	0.031(4)	0.003(3)	0.011(3)	0.002(3)
C(2)	0.035(4)	0.033(4)	0.037(4)	0.003(3)	0.009(4)	0.001(3)
C(3)	0.048(5)	0.029(4)	0.051(5)	0.002(4)	0.017(4)	-0.006(4)
C(4)	0.038(4)	0.050(5)	0.047(5)	0.011(4)	0.012(4)	-0.014(4)
C(5)	0.046(5)	0.061(6)	0.051(6)	-0.001(5)	0.021(4)	-0.010(5)

TABLE 3.3 continued

C(6)	0.043(5)	0.090(8)	0.044(5)	-0.011(6)	0.020(4)	-0.006(5)
C(7)	0.042(5)	0.066(7)	0.049(5)	-0.014(5)	0.017(4)	0.004(5)
C(8)	0.037(4)	0.043(5)	0.041(5)	-0.008(4)	0.013(4)	0.001(4)
C(9)	0.036(4)	0.038(5)	0.028(4)	0.005(3)	0.013(3)	0.005(3)
C(10)	0.036(4)	0.046(5)	0.037(4)	-0.002(4)	0.010(4)	-0.007(4)
C(11)	0.056(5)	0.052(5)	0.033(5)	-0.002(4)	0.018(4)	-0.008(4)
C(12)	0.052(6)	0.071(7)	0.048(5)	-0.010(5)	0.027(5)	-0.001(5)
C(13)	0.037(5)	0.065(7)	0.064(6)	-0.023(6)	0.018(4)	0.010(5)
C(14)	0.058(6)	0.053(6)	0.057(6)	-0.009(5)	0.017(5)	0.016(5)
C(15)	0.057(5)	0.038(5)	0.045(5)	0.002(4)	0.018(4)	0.008(4)
N(20)	0.047(4)	0.038(4)	0.050(4)	0.006(3)	0.016(3)	0.003(3)
C(20)	0.041(5)	0.051(6)	0.052(5)	0.002(5)	0.014(4)	0.002(4)
C(21)	0.064(6)	0.043(6)	0.059(6)	0.009(5)	0.022(5)	-0.006(5)
C(22)	0.044(5)	0.039(5)	0.076(7)	0.005(5)	0.008(5)	0.005(4)
C(23)	0.043(5)	0.047(6)	0.078(7)	-0.003(5)	0.020(5)	0.005(4)
C(24)	0.040(5)	0.048(6)	0.049(5)	-0.006(4)	0.010(4)	-0.001(4)

TABLE 3.4 Bond lengths (Å) for [pyH][Ir($C_{10}H_6NO_2$)pyCl_3]

Ir	-Cl(1)	2.343(2)	Ir	-Cl(2)	2.350(2)
Ir	-Cl(3)	2.364(2)	Ir	-O(2)	2.025(5)
Ir	-N(1)	1.976(6)	Ir	-N(11)	2.099(6)
O(2)	-C(2)	1.300(10)	O(1)	-N(1)	1.274(8)
N(1)	-C(1)	1.352(10)	N(11)	-C(11)	1.351(11)
N(11)	-C(15)	1.344(10)	C(1)	-C(2)	1.416(11)
C(1)	-C(9)	1.465(11)	C(2)	-C(3)	1.421(11)
C(3)	-C(4)	1.350(12)	C(4)	-C(10)	1.431(12)
C(5)	-C(6)	1.354(15)	C(5)	-C(10)	1.411(13)
C(6)	-C(7)	1.394(15)	C(7)	-C(8)	1.386(13)
C(8)	-C(9)	1.404(12)	C(9)	-C(10)	1.426(12)
C(11)	-C(12)	1.376(13)	C(12)	-C(13)	1.410(14)
C(13)	-C(14)	1.366(14)	C(14)	-C(15)	1.354(13)
N(20)	-C(20)	1.350(11)	N(20)	-C(24)	1.331(11)
C(20)	-C(21)	1.356(13)	C(21)	-C(22)	1.379(14)
C(22)	-C(23)	1.368(14)	C(23)	-C(24)	1.365(13)

TABLE 3.5 Bond angles (°) for [pyH][Ir($C_{10}H_6NO_2$)pyCl_3]

Cl(2)	-Ir	-Cl(1)	175.8(1)	Cl(3)	-Ir	-Cl(1)	92.1(1)
Cl(3)	-Ir	-Cl(2)	91.6(1)	O(2)	-Ir	-Cl(1)	89.1(2)
O(2)	-Ir	-Cl(2)	87.3(2)	O(2)	-Ir	-Cl(3)	176.5(2)
O(2)	-Ir	-Cl(2)	87.3(2)	O(2)	-Ir	-Cl(3)	176.5(2)
N(1)	-Ir	-Cl(1)	90.2(2)	N(1)	-Ir	-Cl(2)	91.2(2)
N(1)	-Ir	-Cl(3)	96.3(2)	N(1)	-Ir	-O(2)	80.4(2)
N(11)	-Ir	-Cl(1)	88.8(2)	N(11)	-Ir	-Cl(2)	89.3(2)
N(11)	-Ir	-Cl(3)	89.9(2)	N(11)	-Ir	-O(2)	93.4(2)
N(11)	-Ir	-N(1)	173.8(3)	C(2)	-O(2)	-Ir	111.5(5)
O(1)	-N(1)	-Ir	124.0(5)	C(1)	-N(1)	-Ir	115.3(5)
C(1)	-N(1)	-O(1)	120.6(6)	C(11)	-N(11)	-Ir	120.6(5)
C(15)	-N(11)	-Ir	119.8(5)	C(15)	-N(11)	-C(11)	119.6(7)
C(2)	-C(1)	-N(1)	112.2(7)	C(9)	-C(1)	-N(1)	126.4(7)
C(9)	-C(1)	-C(2)	121.4(7)	C(1)	-C(2)	-O(2)	120.1(7)
C(3)	-C(2)	-O(2)	119.9(7)	C(3)	-C(2)	-C(1)	120.0(7)
C(4)	-C(3)	-C(2)	119.7(8)	C(10)	-C(4)	-C(3)	122.1(8)
C(10)	-C(5)	-C(6)	121.4(9)	C(7)	-C(6)	-C(5)	120.2(9)
C(8)	-C(7)	-C(6)	120.5(9)	C(9)	-C(8)	-C(7)	120.4(8)
C(8)	-C(9)	-C(1)	125.8(7)	C(10)	-C(9)	-C(1)	115.4(7)
C(10)	-C(9)	-C(8)	118.7(7)	C(5)	-C(10)	-C(4)	120.0(8)
C(9)	-C(10)	-C(4)	121.2(7)	C(9)	-C(10)	-C(5)	118.7(8)
C(12)	-C(11)	-N(11)	120.7(8)	C(13)	-C(12)	-C(11)	118.7(9)
C(14)	-C(13)	-C(12)	119.3(9)	C(15)	-C(14)	-C(13)	119.2(9)
C(14)	-C(15)	-N(11)	122.5(8)	C(24)	-N(20)	-C(20)	122.0(8)
C(21)	-C(20)	-N(20)	119.5(8)	C(22)	-C(21)	-C(20)	119.8(9)
C(23)	-C(22)	-C(21)	119.1(9)	C(24)	-C(23)	-C(22)	120.1(9)
C(23)	-C(24)	-N(20)	119.5(8)				

TABLE 3.6 Intermolecular distances (Å) for [pyH][Ir($C_{10}H_6NO_2$)pyCl_3]

H(20n)...Ir	3.63	-2	0.0	0.0	1.0
Cl(1) ...Cl(1)	4.00	-1	1.0	0.0	1.0
C(20) ...Cl(1)	3.69	-1	1.0	0.0	1.0
C(21) ...Cl(1)	3.56	-1	1.0	0.0	1.0
H(20) ...Cl(1)	3.04	-1	1.0	0.0	1.0
H(21) ...Cl(1)	3.07	-1	1.0	0.0	1.0
C(4) ...Cl(1)	3.77	2	1.0	0.0	0.0
H(4) ...Cl(1)	3.04	2	1.0	0.0	0.0
C(6) ...Cl(2)	3.80	-1	1.0	0.0	0.0
C(23) ...Cl(2)	3.68	-1	0.0	0.0	1.0
C(24) ...Cl(2)	3.59	-1	0.0	0.0	1.0
H(24) ...Cl(2)	2.81	-1	0.0	0.0	1.0
H(6) ...Cl(2)	2.84	-1	1.0	0.0	0.0
H(23) ...Cl(2)	2.93	-1	0.0	0.0	1.0
C(14) ...Cl(2)	3.64	2	0.0	0.0	0.0
H(14) ...Cl(2)	2.45	2	0.0	0.0	0.0
C(12) ...Cl(2)	3.75	-2	0.0	1.0	1.0
C(13) ...Cl(2)	3.45	-2	0.0	1.0	1.0
H(13) ...Cl(2)	3.09	-2	0.0	1.0	1.0
C(12) ...Cl(3)	3.75	-1	0.0	0.0	1.0
C(23) ...Cl(3)	3.79	-1	0.0	0.0	1.0
H(12) ...Cl(3)	2.73	-1	0.0	0.0	1.0
H(23) ...Cl(3)	3.09	-1	0.0	0.0	1.0
C(4) ...Cl(3)	3.75	2	1.0	0.0	0.0
C(14) ...Cl(3)	3.76	2	0.0	0.0	0.0

TABLE 3.6 continued

H(4) ...Cl(3)	3.06	2	1.0	0.0	0.0
H(5) ...Cl(3)	3.38	2	1.0	0.0	0.0
H(14) ...Cl(3)	3.29	2	0.0	0.0	0.0
N(20) ...Cl(3)	3.27	-2	0.0	0.0	1.0
C(24) ...Cl(3)	3.41	-2	0.0	0.0	1.0
H(24) ...Cl(3)	2.81	-2	0.0	0.0	1.0
H(20n)...Cl(3)	2.51	-2	0.0	0.0	1.0
C(3) ...O(1)	3.14	2	1.0	0.0	0.0
N(20) ...O(1)	2.74	-2	0.0	0.0	1.0
C(20) ...O(1)	3.04	-2	0.0	0.0	1.0
H(20) ...O(1)	2.71	-2	0.0	0.0	1.0
H(20n)...O(1)	1.92	-2	0.0	0.0	1.0
H(20n)...N(1)	2.91	-2	0.0	0.0	1.0
N(20) ...C(4)	3.40	-1	1.0	0.0	1.0
H(20n)...C(4)	3.05	-1	1.0	0.0	1.0
H(13) ...C(5)	2.91	-2	-1.0	1.0	1.0
C(9) ...C(7)	3.47	-1	1.0	0.0	0.0
N(20) ...C(10)	3.45	-1	1.0	0.0	1.0
H(23) ...C(14)	2.92	-2	0.0	1.0	1.0
C(24) ...C(15)	3.40	-1	0.0	0.0	1.0
H(24) ...C(15)	3.00	-1	0.0	0.0	1.0
H(23) ...C(15)	2.97	-2	0.0	1.0	1.0
H(3) ...C(21)	2.70	-2	0.0	1.0	0.0
H(3) ...C(22)	2.76	-2	0.0	1.0	0.0
H(15) ...C(23)	2.93	-2	0.0	1.0	0.0

TABLE 3.7 Intramolecular distances (Å) for [pyH][Ir($C_{10}H_6NO_2$)pyCl_3]

O(1)	...Ir	2.89	C(1)	...Ir	2.83
C(2)	...Ir	2.78	C(3)	...Ir	4.16
C(11)	...Ir	3.02	C(15)	...Ir	3.00
H(11)	...Ir	3.12	H(15)	...Ir	3.13
Cl(3)	...Cl(1)	3.39	O(2)	...Cl(1)	3.07
N(1)	...Cl(1)	3.07	N(11)	...Cl(1)	3.11
C(1)	...Cl(1)	3.59	C(2)	...Cl(1)	3.57
C(11)	...Cl(1)	3.34	C(21)	...Cl(1)	3.70
H(11)	...Cl(1)	3.24	H(21)	...Cl(1)	2.88
Cl(3)	...Cl(2)	3.38	O(2)	...Cl(2)	3.03
O(1)	...Cl(2)	3.75	N(1)	...Cl(2)	3.10
N(11)	...Cl(2)	3.13	C(1)	...Cl(2)	3.75
C(2)	...Cl(2)	3.63	C(15)	...Cl(2)	3.31
H(15)	...Cl(2)	3.04	O(1)	...Cl(3)	3.22
N(1)	...Cl(3)	3.24	N(11)	...Cl(3)	3.16
C(11)	...Cl(3)	3.22	H(11)	...Cl(3)	2.54
N(1)	...O(2)	2.58	N(11)	...O(2)	3.00
C(1)	...O(2)	2.35	C(3)	...O(2)	2.36
C(15)	...O(2)	3.15	H(3)	...O(2)	2.41
H(15)	...O(2)	2.70	C(1)	...O(1)	2.28
C(8)	...O(1)	2.84	C(9)	...O(1)	2.87
H(8)	...O(1)	2.33	C(2)	...N(1)	2.30
C(8)	...N(1)	3.09	C(9)	...N(1)	2.51
H(8)	...N(1)	2.99	C(12)	...N(11)	2.37
C(13)	...N(11)	2.74	C(14)	...N(11)	2.37

TABLE 3.7 continued

H(11)	...N(11)	2.15	H(15)	...N(11)	2.14
C(3)	...C(1)	2.46	C(4)	...C(1)	2.80
C(8)	...C(1)	2.55	C(10)	...C(1)	2.44
H(8)	...C(1)	2.91	C(4)	...C(2)	2.40
C(9)	...C(2)	2.51	C(10)	...C(2)	2.82
H(3)	...C(2)	2.06	C(9)	...C(3)	2.89
C(10)	...C(3)	2.43	H(4)	...C(3)	2.25
C(5)	...C(4)	2.46	C(9)	...C(4)	2.49
H(3)	...C(4)	2.27	H(5)	...C(4)	2.50
C(7)	...C(5)	2.38	C(8)	...C(5)	2.78
C(9)	...C(5)	2.44	H(4)	...C(5)	2.48
H(6)	...C(5)	2.12	C(8)	...C(6)	2.41
C(9)	...C(6)	2.81	C(10)	...C(6)	2.41
H(5)	...C(6)	2.24	H(7)	...C(6)	2.00
C(9)	...C(7)	2.42	C(10)	...C(7)	2.79
H(6)	...C(7)	2.16	H(8)	...C(7)	2.00
C(10)	...C(8)	2.44	H(7)	...C(8)	1.98
H(8)	...C(9)	2.18	H(4)	...C(10)	2.07
H(5)	...C(10)	2.07	C(13)	...C(11)	2.40
C(14)	...C(11)	2.74	C(15)	...C(11)	2.33
H(12)	...C(11)	2.19	H(22)	...C(11)	2.96
C(14)	...C(12)	2.40	C(15)	...C(12)	2.72
H(11)	...C(12)	2.15	H(13)	...C(12)	2.05
H(22)	...C(12)	2.83	C(15)	...C(13)	2.35
H(12)	...C(13)	2.10	H(14)	...C(13)	2.08
H(13)	...C(14)	2.21	H(15)	...C(14)	2.04
H(14)	...C(15)	2.33	C(21)	...N(20)	2.34
C(22)	...N(20)	2.71	C(23)	...N(20)	2.33

structure resolved for [pyH][Ir(1-nqo)Cl$_3$py] display iridium-chlorine - distance of 2.343(2), 2.350(2) and 2.364 Å.

The results of least square plane calculations show that the quinoneoxime ligand is essentially planar but that the iridium atom is significantly out of this plane.

As was noted earlier, the structure of complexes of quinoneoximes poses several questions. Two fundamental problems considered during this study are (i) whether the metal ligand bond involves the oxygen or nitrogen atom of the NO group and (ii) whether the ligand has the quinoneoxime or nitrosophenol structure in the complex.

The X-ray structure analysis of the complex [pyH][Ir(1-nqo)Cl$_3$py] shows that the ligand anion is co-ordinated to the iridium ion through the nitrogen atom of the NO group and oxygen atom of the CO group. This parallels the observation made by other workers, in the assumption of the five-membered ring alternative. For example, X-ray studies on bis(4-methyl-1,2-benzoquinone 2-oximato)copper(II).monopyridine[6] (Figure 3.5).

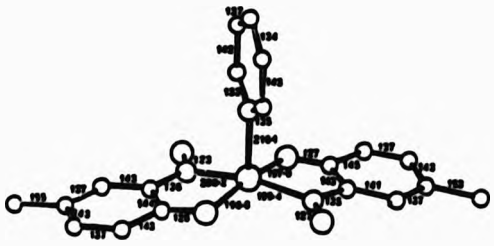


Figure 3.5

and Ferroverdin (Figure 3.6) indicate this type of bonding.[7] This type of bonding has also been established in $Ru(1\text{-}nqo)_2(py)_2$ (Figure 3.7).[21]

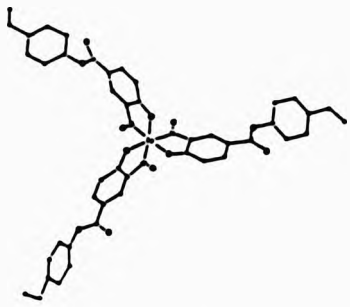


Figure 3.6

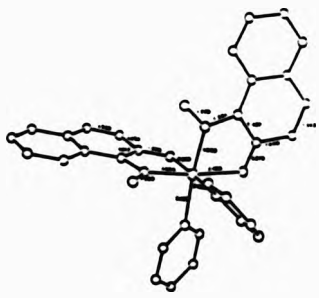


Figure 3.7

However, results of recent X-ray crystallographic studies on the uranyl complexes of 1,2-naphthoquinone mono-oximes $UO_2(2\text{-}nqo)_2(H_2O)_2.2CHCl_3$ and $UO_2(1\text{-}$

nqo)$_2$(Ph_3PO).H_2O show a novel form of bonding not involving five-membered ring formation.[8] The uranyl complex UO_2(2-nqo)$_2$(H_2O)$_2$.2$CHCl_3$ was obtained as a precipitate by the addition of methanolic solution of 1,2-naphthoquinone 2-oxime to an aqueous solution of $UO_2(NO_3)(H_2O)_2 4H_2O$ and was crystallised from chloroform. The structure of the complex depicted in Figure 3.8 demonstrates the bonding in these compounds i.e. the

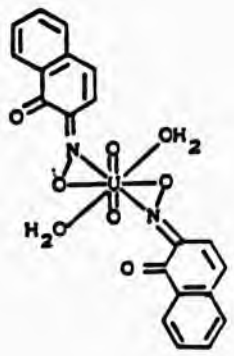
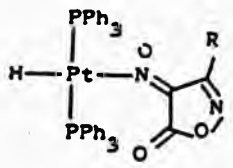


Figure 3.8

co-ordination of the ligand involves both the oxygen and nitrogen atoms of the NO group suggesting η^2 bonding. The water ligand lies in the equatorial plane of the O=U=O group. This parallels observation made for other uranyl complexes. These investigations have demonstrated that uranyl complexes can have 4, 5 or 6 ligand atoms bonded to the uranium in the equatorial plane of the O=U=O group. However, planar 5 and 6 is the most common and appears to give a geometry more stable than the puckered hexagonal configuration. In the complex UO_2(2-

$nqo)_2(H_2O)_2.2CHCl_3$ steric hindrance prevents the 1,2-naphthoquinone 2-oximato ligands from chelating via the nitrogen and ring oxygen atoms. This type of bonding is also a result of the favoured co-ordination number of 6 in the equatorial plane of the O=U=O group[9].

In the complexes of platinum and gold derived from 4-isonitroso-3(R)-isoxazol-5-one[10], the co-ordination of the ligand occurs through the nitrogen of the NO group only (Figure 3.9 & Figure 3.10). This bonding is possible to acquire the most stable configuration for each of the complexes i.e. 4-co-ordinate square-planar geometry for the platinum(II) complex and linear geometry for the gold(I) complex.



R = CH_3 or Ph

Figure 3.9

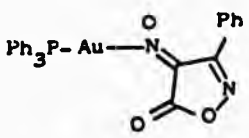


Figure 3.10

Another type of bonding has been observed in potassium 4-chloro-1,2-benzoquinone 2-oximato hemihydrate.[11] In this compound the potassium is bonded to three Clqo ligands through the oximic O atom, and to the other two through the quinonic O, atom as shown in Figure 3.11. No N atom is involved in co-ordination of ligand to the metal.

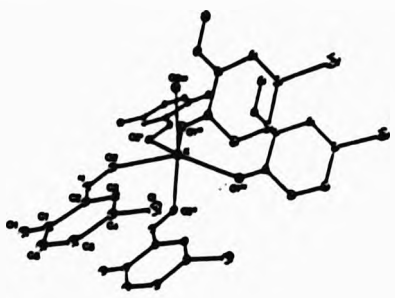


Figure 3.11

Recently, the structure for a lithium complex derived from 1,2-naphthoquinone has been reported.[23] In this complex, Li(1-nqo)(1-nqoH).EtOH, chelation to the metal is via an anionic ligand and a neutral ligand. In this case, the bond lengths for the neutral ligand are very similar to those of the free ligand. For the anionic ligand, the bond lengths agree well with other complexes with anionic ligands.

The X-ray crystallographic studies of complexes derived from 1,2-naphthoquinone monooxime as well as the non-co-ordinated and sulphonated parent ligands are well documented. Some important bond lengths and angles of quinoneoxime complexes and the free protonated 1,2-quinoneoximes are given in Tables 3.8 and 3.9.

In these studies, authors have reasoned that the non-co-ordinated derivatives are quinoneoximic in character involving intramolecular hydrogen bonding. This conclusion was based on the fact that the C - N and N - O bond lengths and CNO bond angles are in accordance with those found in quinones. For example, the quinoneoximic structure in the 1,2-naphthoquinone 1-oxime

Table 3.8 Molecular dimensions of 1,2-quinone monoximes

Compound	C - O (Å)	C - N (Å)	N - O (Å)	$C_3 - C_4$ (Å)	C - N - O (Å)	Ref
1,2-Naphthoquinone-2-oxime-5-sulphonic acid monohydrate	1.24	1.30	1.38	1.33	112.0	12
Potassium 1,2-naphthoquinone-1-oxime-7-sulphonate monohydrate	1.22	1.31	1.39	1.31	114.2	13
6-t-Butyl-1,2-naphthoquinone-1-oxime	1.24	1.30	1.36	1.34	115.9	14
β-5-(2 -Chloroethoxy)-1,2 benzoquinone 2-oxime	1.25	1.31	1.36	1.34	112.3	15
1,2-naphthoquinone 1-oxime	1.25	1.31	1.36	1.33		16

Table 3.9 Molecular dimensions of metal complexes of 1,2 quinone monoximes

Compound	C - O (Å)	C - N (Å)	N - O (Å)	$C_3 - C_4$ (Å)	C - N - O (Å)	Ref
$Cu(1\text{-nqo})_2.2(CH_3)_2CO$	1.29	1.35	1.26	1.36	121.7	17
$Cu(2\text{-nqo})_2.2H_2O$	1.28	1.35	1.26	1.36	121	18
$Cu(1\text{-nqo}).(PPh_3)_2$	1.27	1.37	1.29	1.32	118.2	19
$Cu(4\text{-Meqo})_2.py$	1.28	1.36	1.25	1.37		6
$Ni[(1\text{-nqoS})(H_2O)_4]l\ H_2O$	1.28	1.38	1.26	1.34	120.0	20
$UO_2(1\text{-nqo})(Ph_3PO).H_2O$	1.25	1.33	1.35	1.32	120.0	8
$[pyH][Ir(nqo)Cl_3py]$	1.30	1.35	1.27	1.35	120.6	*
$Ru(1\text{-nqo})_2(py)_2$	1.28	1.38	1.29	1.38		21
$Cu(Clqo)_2.MeOH$	1.28	1.35	1.23			22
	1.27	1.36	1.24			
Li(1-nqo)(1-nqoH).EtOH	1.26	1.33	1.30			23
	1.24	1.28	1.34			

* = This work

ligand is indicated by the short CN(1.31Å), CO(1.25Å), C3-C4(1.33Å) bond distances and the long NO(1.36Å) bond lengths (Figure 3.12).[16] This compares well with those

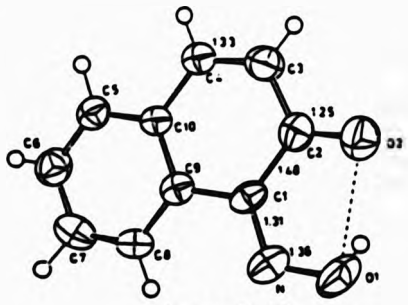


Figure 3.12

found in oximes,[24] for instance, acetoxime (CN,1.29Å; NO,1.36Å) and the CO bond distance with that found in quinones, for example, benzoquinone (CO,1.22Å).[25,26] In 1,2-naphthoquinone 1-oxime the CO and CN bond lengths are longer than the corresponding bonds in 1,2-quinone mono-oximes which do not exhibit intramolecular hydrogen bonding. For example, in 1,2-naphthoquinone 2-oxime 5-sulphonic acid monohydrate the CO and CN bond distances are 1.24Å and 1.30Å respectively (Figure 3.13).[12]

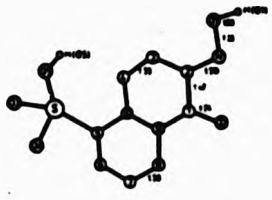


Figure 3.13

All studies of the quinoneoximic complexes indicate that the ligands are quinone oximic in character. This is indicated by the presence of two short and four long C-C bonds in the hexagonal ring of the 1,2-quinone mono-oximato ligands. Furthermore, in all of the complexes, the respective C-O and C-N are shorter than would be expected for a nitrosophenolic structure.

However, the X-ray studies indicate that the co-ordinated ligand anion in the 1,2-naphthoquinoneoxime complexes have the C - N and C - O distances somewhat greater than the free-protonated species (Table 3.8). This is in accord with the shift of the CO absorption in the i.r. spectra, to lower frequency. In addition, there is shortening of the N - O bonds. This is due, at least in part, to the disruption of the H-bonding present in the free ligand.

In the uranyl complex, the CN bond is longer than in the free ligand. In contrast the CO bond, which does not participate in bonding to the metal, is slightly shorter than that of the free ligand.

The X-ray analysis of the iridium complex shows that the ligand anion has C - O, C - N and N - O bond lengths close to those found in other complexes derived from 1,2-naphthoquinone mono-oximes.

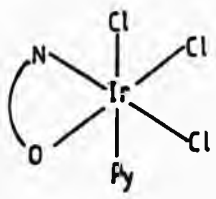
The CO average bond length (1.28 ± 0.01 Å) is longer than that of the free ligand and is in agreement with those observed for the anionic ligands of the copper, ruthenium and lithium complexes. The NO average bond length (1.26 ± 0.01 Å) is shorter than that of the free

ligand and similarly is in agreement with the above metal complexes. The CN average bond length (1.39 ± 0.01 Å) is longer than that of the free ligand which is again in agreement with other metal complexes.

Further evidence for the significance of quinoneoximic contribution is provided by the long C_1-C_2 (1.43 ± 0.01 Å) and the short C_3-C_4 (1.34 ± 0.01 Å) average bond distances.

The bond angles involved in the chelating ligands and metal agree well with other systems (ca 80° for N - Ir-O, 115° for Ir - N - C and 111° for Ir - O - C). Other bond angles in the system are comparable to crystal structures obtained for other metal quinoneoxime complexes.

The interaction of the separate units is very weak and molecules are monomeric in structure. The pyridine molecule and the three chlorines complete the distorted octahedral arrangement around iridium(III) ion. This can be seen by the fact that the Cl - Ir - Cl bond angles are not equal to the idealised value of 90° for octahedral complexes. The molecule adopts a trans isomeric conformation with the pyridine on the opposite side of the ligand anion. The cis- and trans- isomerisation is not unusual, as mentioned in the previous chapter, oxalato complexes exist in isomeric forms (Figure 3.14 & Figure 3.15).



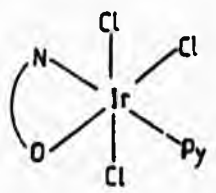


Figure 3.14 Figure 3.15

In the complex under study, the average metal-pyridine bond length (2.10Å) is identical to that observed in the complex $Ru(1\text{-nqo})_2(py)_2$ (2.10Å) and that of the average metal - 2,2'-bipyridyl bonds, in the complex $Cu(qo)_2$ (bipy) (2.10Å). The similarity of the average metal-pyridine (M-N) bond lengths for the above complexes is noteworthy. Although the atomic radius of the atoms of the 1st, 2nd and 3rd row transition elements increase respectively, the metal-pyridine average bond length remains constant.

Comparison of the bond lengths and angles of non-coordinated ligand and co-ordinated states has shown some systematic changes to occur upon co-ordination, but the quinoid character is still significant in representing the structure of the metal complex.

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CHAPTER FOUR

METAL COMPLEXES DERIVED FROM 1,2-NAPHTHOQUINONE-1-OXIME-3,6-DISULPHONIC ACID (NITROSO-R-SALT)

4.1 Introduction

Metal complexes of nitroso-R-salt (1,2-naphthoquinone-1-oxime-3,6-disulphonic acid, disodium salt) have been known for a long time. Immediately after the description by Illinsky[1] of the reaction which takes place between cobalt and 1,2-naphthoquinone-2-oxime, Hoffman[2] observed in 1883 that 1,2-naphthoquinone 2-oxime-4 sulphonic acid gave red colour with cobalt and green with iron. The former was found to be a valuable dyestuff; wool and silk were dyed clear-red from an acid bath.

Nitroso-R-salt is normally prepared easily, with excellent yield by the action of nitrous acid upon the disodium salt of 2-naphthol-3,6-disulphonic acid. The nitrosation reaction is carried out by acidifying cooled aqueous solutions of this salt containing equivalent amounts of sodium nitrite with hydrochloric acid. Recrystallisation of the precipitated nitroso-R-salt from water gives a dihydrate.

An X-ray crystallographic study of the closely related compound, potassium 1,2-naphthoquinone 1-oxime-7-sulphonate monohydrate indicates that the CN(1.31 Å), NO(1.39 Å), CO(1.22 Å), and C_3-C_4(1.31 Å) bond lengths are relatively short (cf. Chapter 3), suggesting that the organic anion exists in the oximic form (Figure 4.1).[3] From the structure it can also be deduced that

this compound arises by the loss of the acidic hydrogen of the sulphonic group.

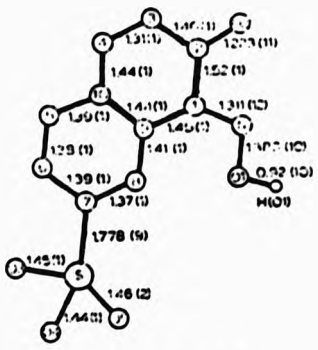

Figure 4.1

By analogy, it is reasonable to assume that in the nitroso-R-salt (i.e. 1,2-naphthoquinone 1-oxime-3,6-disulphonic acid, disodium salt), the sodium ions are associated with the sulphonic groups and that that anion has oximic character (Figure 4.2).

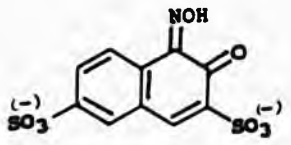

Figure 4.2

An oximic structure is also indicated for 1,2-naphthoquinone 1-oxime 3,6-disulphonic acid. In this compound in addition to the replaceable hydrogen of the oxime group there are also two other acidic hydrogens due to the sulphonic groups. As a consequence in this thesis the abbreviation $nRsH_3$ will be used for 1,2-naphthoquinone 1-oxime-3,6-disulphonic acid. On this basis the Nitroso-R-salt will be abbreviated as $nRsHNa_2$.

The chelating behaviour of the sulphonated derivatives of 1,2-naphthoquinone 1-oxime towards transition metals is similar to that of the parent oxime (i.e. 1-nqoH). The chelation occurs through the nitrogen of NO group and oxygen of the CO group to form a five-membered ring as shown by the crystal structure of tetra-aqua (1,2-naphthoquinone 1-oximato-6-sulphonate)nickel(II) (Figure 4.3).[4] Significantly, in this complex the ligand behaves as a dianion and its formation involves loss of both the oximic and sulphonic group hydrogens.

Figure 4.3

4.2 Complexes of 1,2-Naphthoquinone-1-oxime-3,6-disulphonic acid

The formation of metal complexes derived from 1,2-naphthoquinone- -oxime-3,6-disulphonic acid has been extensively investigated for analytical purposes.[5-11] For example, cobalt can be quantitatively determined in the presence of 200 times its weight of nickel. Table 4.1 gives some examples and proposed formulation of complexes derived from 1,2-naphthoquinone- -oxime-3,6-disulphonic acid and related ligands. These formulations are rather superficial and at best indicate the metal to ligand ratio. This is because they are generally based on solution studies. Previously the isolation of the complexes in the solid state has not been attempted except in the case of the rhodium complex.[33]

In this study it has been possible to isolate cobalt, rhodium, iron, copper and nickel complexes of 1,2-naphthoquinone 1-oxime-3,6-disulphonic acid, in the solid state. All the complexes were prepared by the reaction of the metal chloride and nitroso-R-salt in water. In contrast, under similar conditions no reaction was observed between the nitroso-R-salt and zinc(II) or manganese(II) chlorides. The copper complex was isolated readily as it precipitated out from the reaction mixture. In contrast the cobalt, rhodium and iron complexes were soluble in water and a special technique for the isolation of the solid had to be developed.

TABLE 4.1 Some complexes of sulphonated derivatives of 1,2-naphthoquinone 1-oxime.

Metal	Ligand	Proposed metal/ligand ratio	Basis of formulation	Ref
Co	L1	1:3	a,b,c	5 12-18
Co	L1	1:2	b,c	18
Co	L1	1:1	b,c	18
Fe	L1	1:3	b,c	5,19-25
Fe	L2	1:1	b,c	26-30
Ni	L1	1:1	b,c	26-30
Ni	L2	1:1	x-ray	4
Ni	L3	1:1	b,c	27
Ni	L4	1:1	bc	27
Cu	L1	1:1	b,c	5,30
Cu	L1	1:2	b,c	5,30
Cu	L2	1:2	b,c	30
Cu	L2	1:1	b,c	30
Zn	L2	1:1	b,c	31
Zn	L2	1:2	b,c	31
Rh	L1	1:3	a,b,c	32,33

L1 = 1,2-naphthoquinone 1-oxime-3,6-disulphonic acid
L2 = 1,2-naphthoquinone 1-oxime-6-disulphonic acid
L3 = 1,2-naphthoquinone 1-oxime-7-disulphonic acid
L4 = 1,2-naphthoquinone 1-oxime-3-disulphonic acid
a = Metal analysis
b = Kinetic formation and dissociation
c = Spectroscopic technique

4.2.1 Reaction of Cobalt(II) Chloride with Nitroso-R-salt

On mixing a solution of nitroso-R-salt with a cobalt(II) chloride solution there was a rapid colour change as observed previously.[12-17] Isolation of the resultant cobalt complex was achieved by concentrating the solution to a small volume, adding silica to the mixture, and then extracting the complex from the silica with methanol. Removal of the solvent from the methanol extract gave a red coloured solid. The elemental analysis of the product, which was obtained in good yield, corresponds very closely to a cobalt:ligand ratio of 1:3 and suggests the formulation $Co(nRsNa_2)_3.5H_2O$. This ratio, the colour of the complex and the i.r. are similar to the corresponding features of the product $Co(1\text{-}nqo)_3$ obtained from the reaction of cobalt(II) chloride with 1,2-naphthoquinone 1-oxime.[34] The product was shown to be diamagnetic as determined by magnetic susceptibility measurements. This diamagnetism is in keeping with the presence of low spin cobalt(III), thus confirming the formulation as $Co(nRsNa_2)_3$.

4.2.2 Reaction of Rhodium(III) Chloride with Nitroso-R-salt

When nitroso-R-salt was mixed with hydrated rhodium(III) chloride in water at 20°C reaction proceeded very slowly. On heating, rapid change of colour was observed. Isolation of the complex, achieved as above, gave reddish-orange $Rh(nRsNa_2)_3.3H_2O$ in low yield. The

purification was achieved as for the cobalt complex. The formulation was based on full elemental analysis and the diamagnetic character of the product which indicates a rhodium(III) species. The complex had well-defined i.r. spectrum which compared well with i.r. spectrum of the cobalt complex. The solid was extremely soluble in water and slightly soluble in methanol. The slow reaction between nitroso-R-salt and rhodium(III) was also noted by other workers and can be related to the inertness of Rh(III) ions. Previously other workers reported the formation of a blue product from the reaction of nitroso-R-salt with rhodium(III) sulphate but failed to isolate it.[32] Other workers obtained a red product which they formulated as $Na_6[Rh(C_{10}H_4NO_2(SO_3)_2]_3 . NaSO_4 . 11.5\ H_2O$.[33] This formulation may be presented as $Rh(nRsNa_2)_3\ NaSO_4 .11\ H_2O$ which apart from the presence of some '$NaSO_4$' is similar to the formulation proposed in this study.

4.2.3 Reactions of Copper(II) Chloride with Nitroso-R-salt

The interaction of nitroso-R-salt with copper(II) chloride in 1:1 reactant ratio gave a copper-containing solid as a brown precipitate. Elemental analysis of the product, which resulted in high yield, indicated a ligand:copper:sodium ratio of 1:1:1 and suggested formulation $Cu(I)(nRsHNa).10H_2O$ or Cu(II) (nRs Na) $10H_2O$.

Initially the formulation of the product as a copper(I) species seemed to be appropriate as the compound was found to be diamagnetic. However, there was no evidence of ligand oxidation which is expected to accompany the reduction of copper.

The formulation of the product as Cu(II)(nRs Na)$1OH_2O$ involves a formally dianionic ligand. Such behaviour is analogous to that observed for the nickel(II) complex derived from 1,2-naphthoquinone 1-oxime-6-sulphonic acid whose structure has been established by X-ray crystallography (cf. Introduction). Diamagnetism or generally subnormal magnetic behaviour in copper(II) complexes is known and is due to association which leads to a magnetically concentrated system. In a complex of formula Cu(II)(nRs Na).$10H_2O$ association can occur in a variety of ways and some evidence for association is indeed provided by the insolubility of the complex.

On the basis of the above, formulation of the product as a copper(II) species seems to be the most likely. The compound reacted readily with pyridine to give a pyridine adduct of formulation Cu(nRs Na)$(py)_2(H_2O)_2$ which was also found to be diamagnetic.

4.2.4 Reactions of Iron(II) or Iron(III) Chlorides with Nitroso-R-salt

Reaction of nitroso-R-salt with iron(II) chloride in water afforded a green solution from which a green, highly hygroscopic, iron complex of formulation Fe(nRs Na) $5H_2O$ was isolated, following a procedure analogous to

that described for the cobalt complex.

As for copper, the metal:ligand ratio is 1:1 and the proposed formulation implies the involvement of Fe(II). The presence of iron(II) is supported by the colour of the complex as previously many iron(II) quinone oximate complexes e.g. $Fe(qo)_2$ (qoH=1-nqoH, 2-nqoH, 5-MeqoH) were found to be dark green in colour. The room temperature magnetic moment of the complex was found to be 2.2B.M. which is low for a magnetically dilute iron(II) species. The subnormal magnetic moment is comparable for values reported for iron(II) complexes of type $Fe(qo)_2$ and is caused by the association between neighbouring $Fe(qo)_2$ units (Figure 4.4).[35]

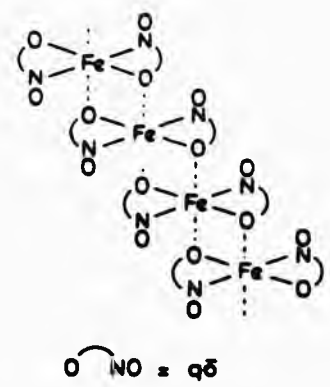

Figure 4.4.

When nitroso-R-salt was reacted with iron(III) chloride in water a brown solution was formed which gradually developed a green colour. This observation has also been made in the preparation of other Fe(III) quinone oximic complexes and it has been suggested that

internal redox of the initially formed brown iron(III) complex gives a green iron(II) complex. The green solution obtained was mixed with silica and the solvent was removed. Extraction of the coated silica with methanol and removal of the solvent gave a green Fe(II) product of formulation Fe(nRs Na).$5H_2O$ which is similar to the product obtained from the reaction between iron(II) chloride and nitroso-R-salt.

The reaction of nitroso-R-salt with iron(II) ammonium sulphate was also investigated. The product, a green solid, was isolated using the silica method. The i.r. of the solid was similar to those of the products obtained from the reactions of nitroso-R-salt with iron(II) or iron(III) chloride. However, the elemental analysis indicated a metal to ligand ratio of 1:2 and the content of nitrogen was high. The high N content implies that NH_4 ion or ammonia are present, indicating possible formulations depicted in Figure 4.5 and Figure 4.6.

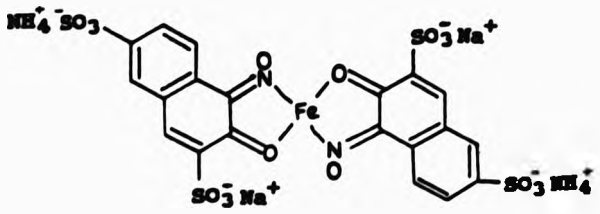

Figure 4.5

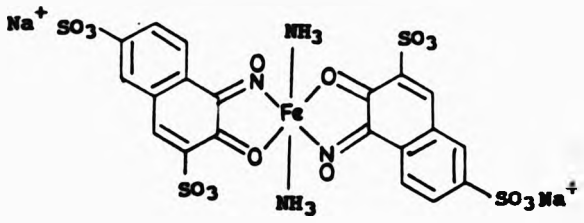

Figure 4.6

The observed magnetic moment 4.45B.M. is in accord with high spin Fe(II) species which involves some interaction between neighbouring Fe(NnRs Na) units. On this basis, structure proposed in Figure 4.5 is more likely, as structure shown in Figure 4.6 does not allow interaction.

4.2.5 Reaction of Nickel(II) Chloride with Nitroso-R-salt

Reaction of nitroso-R-salt with nickel(II) chloride in water afforded a mixture. Filtration gave a unreacted nRsHNa as a yellow residue and a brown filtrate. Evaporation of the filtrate gave a brown solid. The brown solid was purified by adding silica and washing the coated silica with methanol. Removal of the solvent from the methanol extract resulted in a brown solid. The elemental analysis of the product, which was obtained in good yield, corresponds to nickel:ligand of 1:2 and indicated the formulations $Ni(nRsHNa)_2 5H_2O$. The room temperature magnetic moment of the complex was found to be 2.83 B.M. This is in agreement with the value expected for an octahedral nickel(II) complex.

4.3 Conclusion

For the complexes, namely $Co(nRsNa_2)_3 5H_2O$, $Rh(nRsNa_2)_3 H_2O$, $Fe(nRsHNa)_2\ 5H_2O$ and $Ni(nRsHNa)_2\ 5H_2O$ reasonable structural suggestions have been made. In all these cases, the ligand is chelating to the metal via the nitrogen atom of the oxime and the oxygen atom of the quinone groups and sodium ion or ammonium ion are associated with one or two of the sulphonate substituents. The i.r. spectra of cobalt, rhodium and nickel complexes of 1,2-naphthoquinone 1-oxime-3,6-disulphonic acid bear similarities with the i.r. spectra of the complexes derived from the parent ligand, 1,2-naphthoquinone 1-oxime . That is, the i.r. spectra show typical peaks associated with chelated 1,2-naphthoquinone 1-oximato anions, e.g. 1610-1500 cm^{-1} (Figures 4.7 - 4.14). This indicates the involvement of the carbonyl and the oximic functions in the chelation. The i.r. spectra of the iron complex obtained from the reaction between iron(II) or iron(III) chloride and nitroso-R-salt, and the complex of copper show close similarities to the i.r. of other complexes of nitroso-R-salt. It is thus reasonable to assume that in these cases the ligand co-ordinates to the metal in an analogous fashion. In addition, the formation of the $Cu(nRs\ Na)10H_2O$ and $Fe(nRs\ Na)5H_2O$ involves both the oximic and the sulphonic sites of the ligand thus leading to the formulation metal to ligand ratio of 1:1. Unfortunately, no structural suggestions can be made with any degree of certainty. Generally, it has been established that the reactivity

between 1,2-naphthoquinone 1-oxime-3,6-disulphonic acid ligand and metal salts is complex.

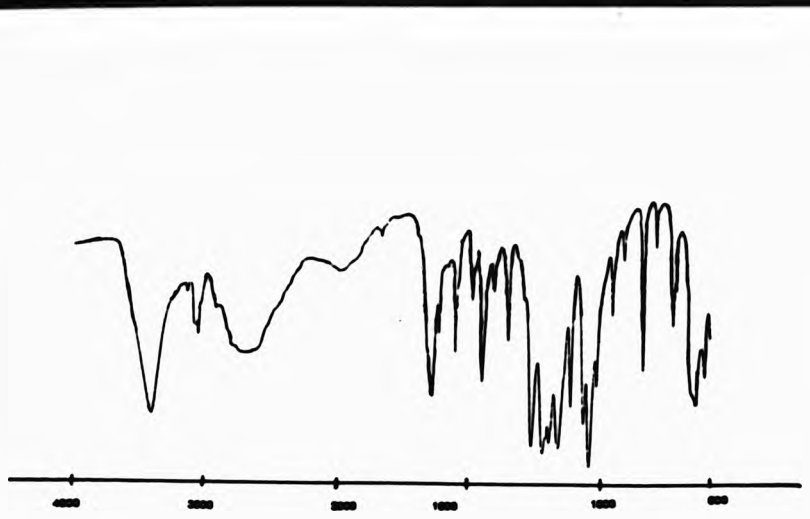

Figure 4.7 Infra-red spectrum for $nRsHNa_2$

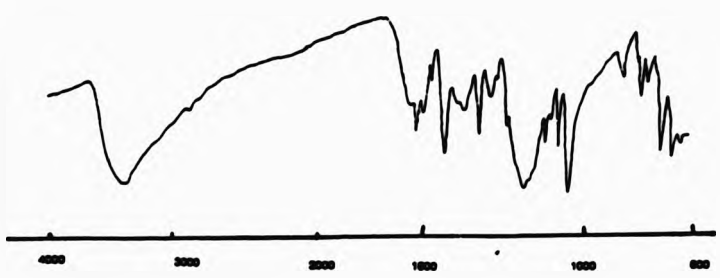

Figure 4.8 Infra-red spectrum for $Co(nRsHNa)_3 5H_2O$

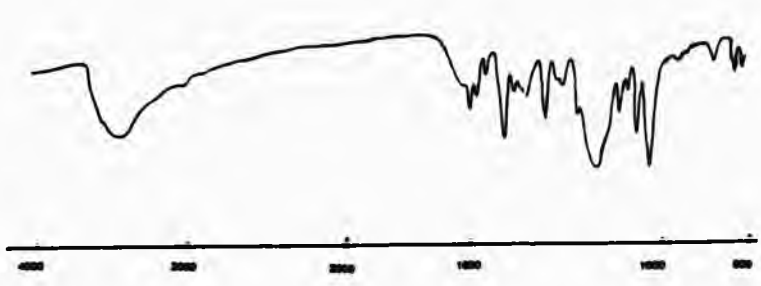

Figure 4.9 Infra-red spectrum for $Rh(nRsHNa)_3H_2O$

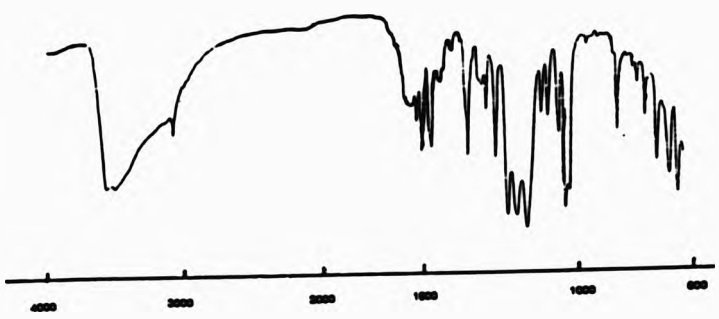

Figure 4.10 Infra-red spectrum for $Cu(nRs\ Na)10H_2O$

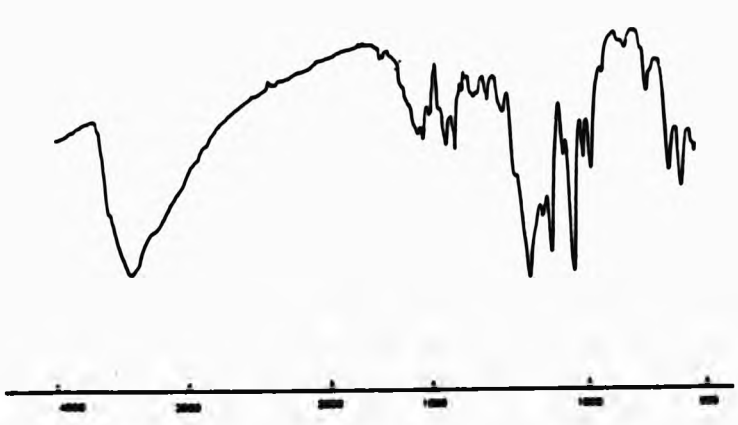

Figure 4.11 Infra-red spectrum for $Fe(nRs\ Na)\ 5H_2O$

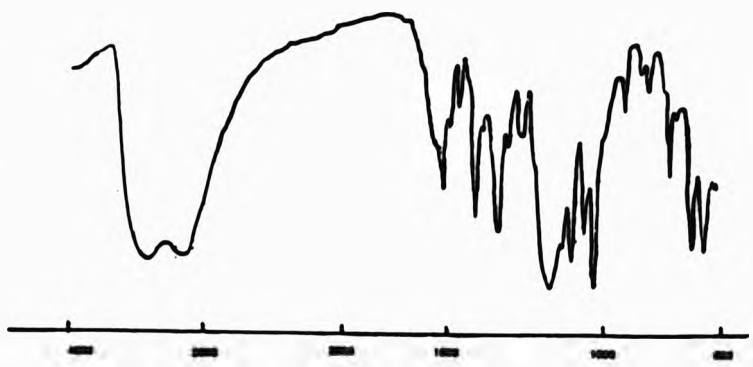

Figure 4.12 Infra-red spectrum for $[NH_4]_2[Fe(nRs\ Na)_2]2H_2O$

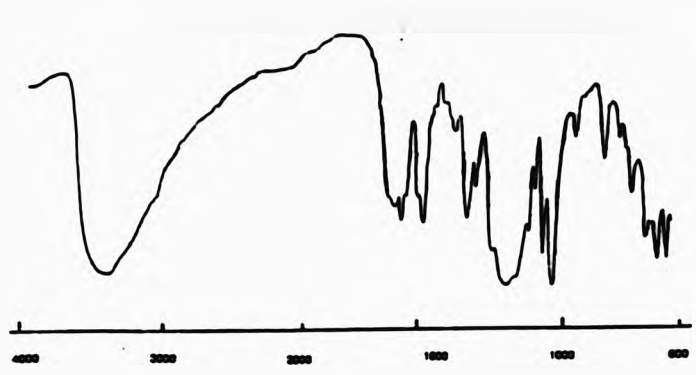

Figure 4.13 Infra-red spectrum for $Ni(nRsHNa)_2 5H_2O$

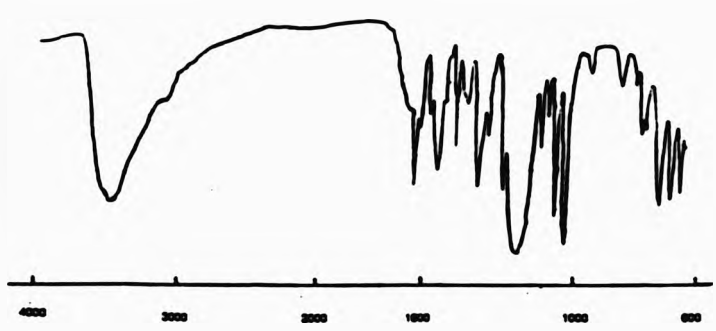

Figure 4.14 Infra-red spectrum for $Cu(nRs\ Na)(py)_2(H_2O)_2$

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CHAPTER FIVE

SEPARATION OF RHODIUM(III) AND IRIDIUM(III) USING 1,2-NAPHTHOQUINONE MONO-OXIMES

5.1 Introduction

Platinum metals in the past were used in the jewellery and decorative trades and in recent years have been used in the glass, heavy chemicals and petroleum industries. These metals have certain ideal properties for use in industry, e.g. high melting points and corrosion resistance. They have been used as catalysts for the removal or conversion of polluting gases. The processes used to separate and purify these metals are long and not very efficient so improvements are highly desirable.

The application of solvent extraction techniques to the separation of metals has allowed considerable improvements in efficiency to be achieved. Metals can be extracted selectively and sequentially and almost complete separation is possible. A common method of achieving extraction involves co-ordination of the metal with a suitable ligand soluble in organic solvents. Scrubbing of the loaded organic phase serves as a purification operation, so that strip liquor yields pure salt, and hence pure metal directly. Scrub liquors containing the free ligand, however, then represent recycle streams.

The refinery operations have a number of distinct disadvantages including inefficiency of precipitation procedures: coprecipitation of impurities; large number of stages involved; and tie-up of capital due to length

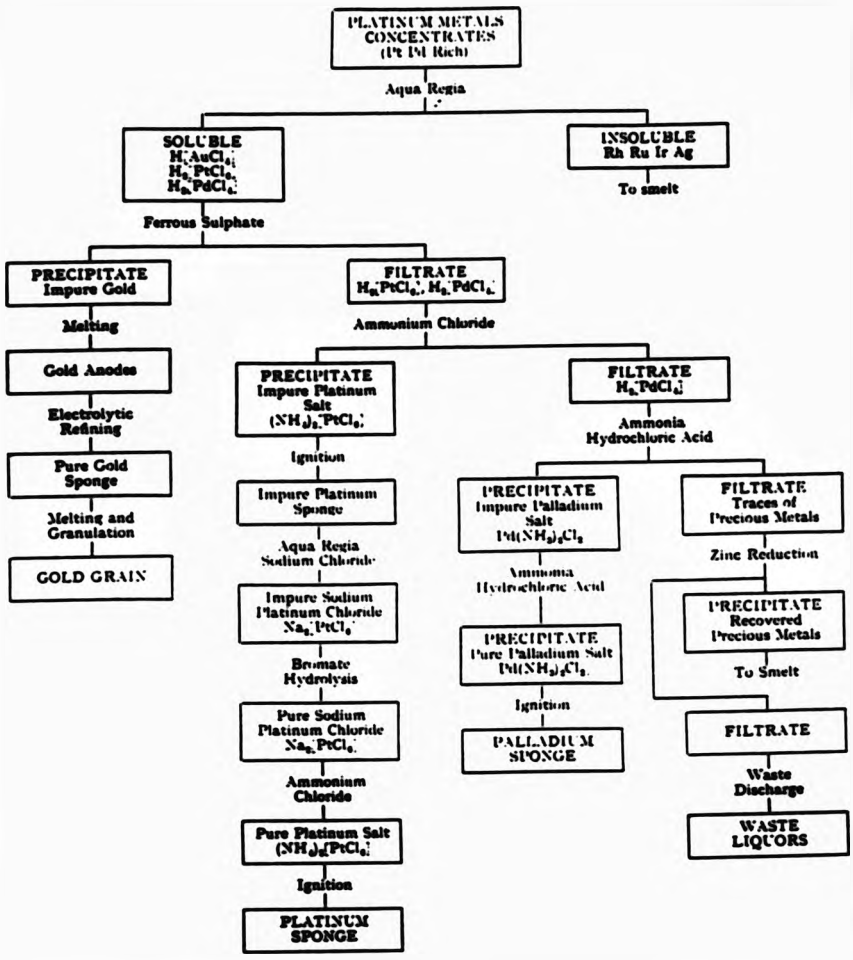

Figure 5.1

The classical refining process at Inco's Acton refinery for platinum group metal concentrates rich in gold, platinum and palladium.

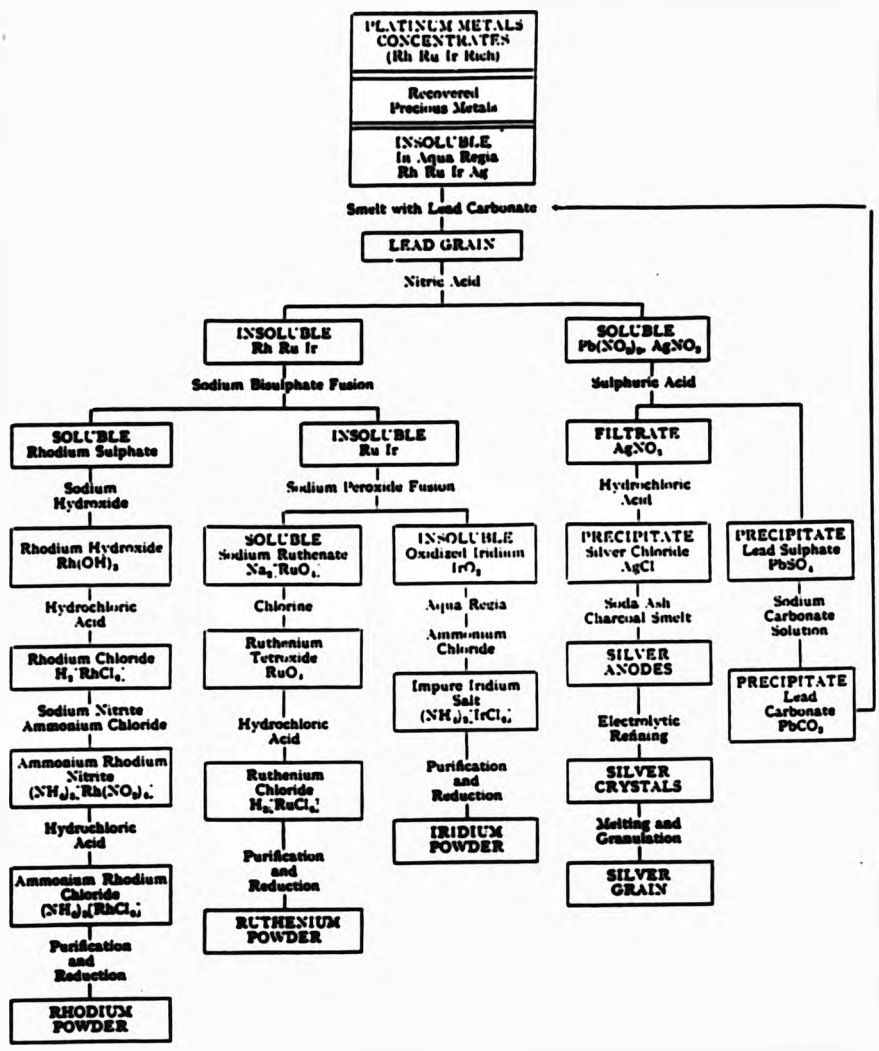

Figure 5.2

The classical process route at Inco's Acton refinery for platinum group metal concentrates rich in rhodium, ruthenium, iridium and osmium.

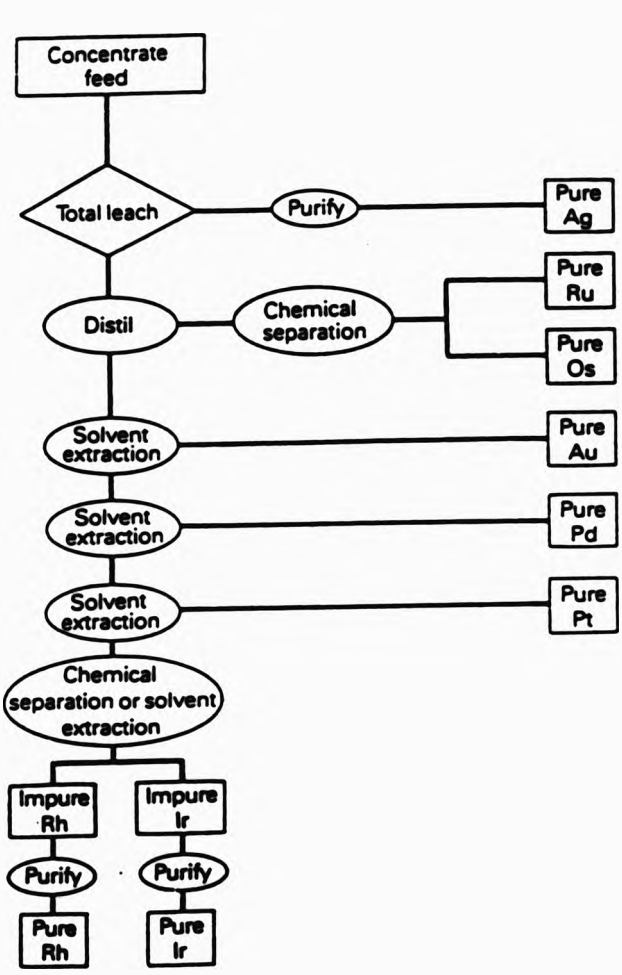

Figure 5.3

Solvent extraction process at Inco's Acton refinery

of procedures.

The aim of this work was to devise and develop a procedure for the separation and purification of rhodium and iridium by using 1,2-naphthoquinone 1-oxime and a suitable diluent to extract rhodium selectively in relation to iridium and then recovering the metal.

5.2 Current Process at Inco

The precious metals occur in nature in ores containing the nickel mineral pentlandite [$(Fe,Ni)_9S_8$], the copper mineral chalcopyrite ($CuFeS_2$) and the iron mineral pyrrhotite (Fe_7S_8). Small amounts of other minerals e.g. sperrylite ($PtAs_2$) are also present in the deposit. Substantial amounts of these ores occur in Ontario and Manitoba, Canada, and are mined by International Nickel Co Ltd.

After electrolyte refining of the major constituents the precious metals are found in the form of slimes, and the involatile residue from the carbonyl process which are collected and concentrated. These precious metal concentrates are sent to the Precious Metal Refinery at Acton, West London, where the individual metals are separated and purified. Although the original ores contain only trace amounts of precious metals, the very large tonnage mined each year and the efficiency of the concentration process lead to the production of an appreciable proportion of the platinum metals available.

The refining process was based upon a primary separation between PMs soluble in aqua regia, viz.

platinum, palladium and gold and those present in an insoluble form (rhodium, iridium, ruthenium, osmium, silver). The classical refining scheme proceeds as shown in the simplified flowsheet in Figure 5.1 and Figure 5.2. Details of these stages have been described by Clements [1] and other workers.[2,3]

The method of selective leaching followed by repeated precipitation and recrystallisation gives poor first time yields and is often time-consuming because of the need to handle solids. This results in a significant inventory or lock up of PMs in process intermediates. This is an important factor in the operating economics of PM refining because of the high cash value of the metals held up. As a consequence, the potential of solvent extraction was recognised and first applied to gold refining.[4] There is a considerable improvement in the recovery of gold by solvent extraction in comparison with the conventional method. The classical method involved the use of large quantities of ferrous sulphate followed by electrolysis. The method not only inhibited subsequent precipitation of PMs but it was time-consuming.

The present process involves the total leaching of the concentrates and the elements are solvent extracted selectively and sequentially from the total leach liquor, Figure 5.3. After separation of ruthenium and osmium by distillation of their tetraoxides, the solution is solvent extracted with di-butyl carbitol to extract gold. Recovery of gold from the laden organic phase is by

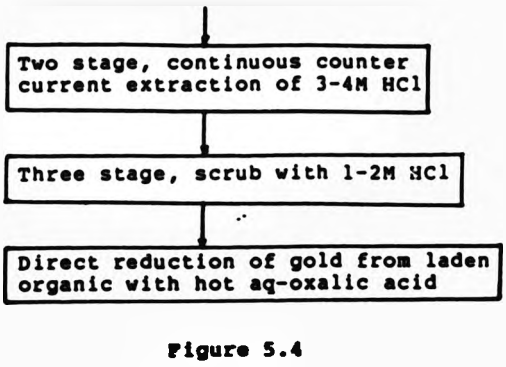

Figure 5.4

Process for solvent extraction of gold with di-butyl carbitol (di-ethyleneglycol dibutyl ether).

direct reduction with aqueous oxalic acid. There is no conventional stripping stage, Figure 5.4. The gold-free raffinate is then solvent extracted with di-n-octyl sulphide (DOS) in Esso Isopar M, an aliphatic hydrocarbon diluent, which selectively extracts palladium (Reaction 5.1).

$$[PdCl_4]^{2-}_{aq} + 2[R_2S]_{org} \rightleftharpoons [PdCl_2(R_2S)_2]_{org} + [2Cl]^-_{aq}$$

(Reaction 5.1)

The loaded organic phase is scrubbed with HCl and then stripped with aqueous ammonia to form $[Pd(NH_3)_4]^{2+}$ (Reaction 5.2). Neutralisation with HCl gives insoluble $Pd(NH_3)_2Cl_2$ salt (Reaction 5.3) which can be converted to pure metal by reduction with formic acid (Reaction 5.4).

$$[PdCl_2(R_2S)_2] + 4[NH_3] \rightleftharpoons [2R_2S] + [Pd(NH_3)_4]^{2+} + 2[Cl]^-$$

(Reaction 5.2)

$$[Pd(NH_3)_4]^{2+} + 4HCl \longrightarrow Pd(NH_3)_2Cl_2 + 2NH_4Cl$$

(Reaction 5.3)

$$Pd(NH_3)_2Cl_2 + HCOOH \longrightarrow Pd + CO_2 + 2NH_4Cl$$

(Reaction 5.4)

Solvent extraction of platinum is achieved by using tri-n-butyl phosphate (TBP). The extraction is greatest at 5M HCl and the scrubbing to remove traces of co-extractant impurities is with 5-6M HCl. The organic phase is stripped at approxi mately 0.5M HCl and platinum metal is recovered from the stripped liquor by precipitation of $(NH_4)_2PtCl_6$ with ammonium chloride.

One of the oldest methods for separating rhodium and iridium which was used at the Acton refinery until recently, involves fusing the mixture of metals with sodium bisulphate; rhodium forms water soluble sulphate while iridium remains as the metal. The method is tedious and does not produce a complete separation of the elements.

Rhodium and iridium can also be separated by chlorinating a mixture of the two in the presence of

sodium chloride followed by the separation of iridium with a mixture of acetone and ether. This method does not yield a satisfactory separation and the flammability of these solvents is a severe disadvantage in today's safety-conscious industry.

Iridium is now removed from rhodium by precipitating $(NH_4)_2[IrCl_6]$ but the separation is incomplete because of the appreciable solubility of ammonium chloroiridate(IV) and because of co-precipitation of $(NH_4)_3RhCl_6$ if the liquor is very rich in rhodium, Figure 5.5. Selective reduction of rhodium to the metal with various reducing agents has been suggested. However, the use of reducing agents such as titanium(III) salts, chromium(II), vanadium(III), mercury(I) salts or metallic copper is always accompanied by contamination of rhodium and iridium by these metals, thus necessitating further purification.

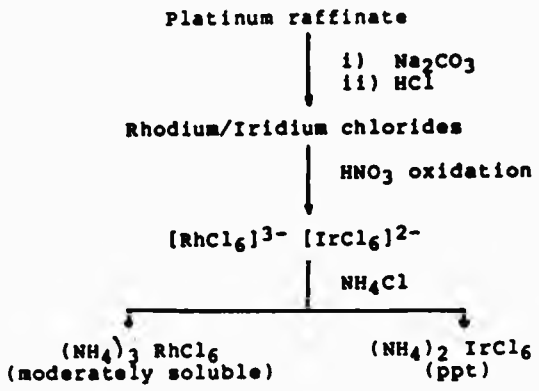

Figure 5.5

Present procedure at Inco's Acton refinery for separating rhodium and iridium.

The redissolution of rhodium metal is slow which counts against any procedure requiring its formation and redissolution for the purpose of further purification.

The use of organic reagents has also been recommended for the selective precipitation of the elements. The advantage of methods employing organic reagents to separate rhodium and iridium over methods involving selective reduction of rhodium(III) to the metal lies in the possible easy redissolution of the precipitate. The ability of some of the resulting compounds to dissolve in organic solvents allows solvent extraction techniques to be used. The number of organic reagents available for the extraction of iridium is very limited in comparison to the number available for the other PMs. The method with p-nitrosomethylaniline is non-selective and this is true for other organic reagents. The precipitation of iridium and rhodium with 1-(2-pyridylazo)-2-naphthol (PAN) and hydroxyquinoline occurs simultaneously. Table 5.1 shows some of the organic reagents used for extraction of rhodium and iridium.

The selective precipitation of rhodium with certain sulphur containing organic reagents in the presence of strong reducing reagents such as titanium(III) salts, chromium(II) is also of interest. In these cases rhodium is allowed to be reduced to a lower oxidation state which forms stable compounds with the organic reagent. The thioacetanilide compound of rhodium has been isolated in the presence of chromium(II).

Table 5.1 Some examples of extractants used for separation of Rh(III) and Ir(III)

Metal	Extractant	Conditions	Ref.
Ir(III)	Theinoyltrifluoroacetone	pH 8.5, 0.015M HTTA in benzene	5, 6
Ir(III)	8-Mercaptoquinoline	pH 7.6-9.0 - heating	7
Ir(III)	1-(2-Pyridylazo)-2-naphthol	pH 5.1 - heating 1h with ethanolic PAN	8
Rh(III)	Theinoyltrifluoroacetone	pH 6, 0.015M HTTA	5, 6
Rh(III)	8-Hydroxyquinoline	pH 6-8 - heating	8
Rh(III)	8-Mercaptoquinoline	pH 5-6 - heating	7
Rh(III)	1-(2-Pyridylazo)-2-naphthol	pH 5.1 - heating	8

5.3 Separation of rhodium from iridium with 1,2-naphthoquinone mono-oxime

During this study, it has been shown that rhodium(III) chloride reacts with 1,2-naphthoquinone mono-oxime under various conditions to give several products. Refluxing hydrated rhodium(III) chloride with 3 molar equivalents of 1,2-naphthoquinone mono-oxime for one hour in methanol buffered to pH 4-5 with acetic acid gave a near quantitative yield of the neutral trischelate $Rh(1\text{-nqo})_3$. Similar reactions with chloroiridic(IV) acid which had been reduced to iridium(III) chloro complexes with propan-2-ol gave a mixture of products after refluxing for five days.

The above results suggest that a mixture of rhodium and iridium may be separated by exploiting the faster rate at which rhodium reacts with quinone mono-oxime in weakly acid solutions. In order to access the validity of this hypothesis and evaluate its potential, a systematic study of the factors affecting the separation of rhodium and iridium using 1-nqoH was undertaken. The factors investigated were a) heating time, b) pH, c) amount of reagent. It was anticipated that optimum conditions for the separation of rhodium could be determined.

5.3.1 Effect of heating time and temperature

In this set of experiments an aqueous solution of 1,2-naphthoquinone 1-oxime was added to an aqueous solution of rhodium(III) and iridium(III) of required pH.

The results for the dependence of the rhodium precipitation on heating time are presented in Table 5.2. It was established that no reaction or very little reaction occurred when stirred at room temperature, even after stirring for several days. For heating times at reflux temperature of 0.5, 1.0, 1.5 and 5.0 h using a reagent concentration of 0.003M, the percentages of rhodium extracted at pH 5.0 - 5.5 were 68, 80, 96 and 98% respectively.

At 70°C the reaction became apparent and red spongy precipitate began to float. Near the boiling point, the solution was totally diffused with reddish brown solid. It is clearly evident that the complete precipitation occurs on continuous heating at reflux temperature rather than at lower temperatures. It can also be deduced from Table 5.2 that prolonged heating at reflux temperature (>5 h) tends to precipitate small amounts of iridium as well. The lack of reactivity at room temperature is partly due to the limited solubility of 1,2-naphthoquinone 1-oxime in water. Thus the formation of the precipitate depends to a large extent on the heating period. The optimum time of heating would be between 1.5 - 5.0 h.

5.3.2 Effect of the amount of reagent used

Table 5.3 shows the dependence of the separation of rhodium(III) on the amount of reagent used. It was observed that on addition of excess 1,2-naphthoquinone

Table 5.2 The effect of time and temperature on the precipitation of rhodium(III)[a]

Time (h)	20°C		70°C		Reflux Temp	
	Rh	Ir	Rh	Ir	Rh	Ir
	(wt. in aqueous layer, mg)		(wt. in aqueous layer, mg)		(wt. in aqueous layer, mg)	
0.5	50	50	32.1	50.2	16.6	49.2
1.0	50	50	20.4	49.1	10.1	47.5
1.5	50	50	14.4	48.7	1.5	46.8
5.0	50	50	10.8	46.4	0.87	42.1

a = weight of starting materials: Ir = 50mg; Rh = 50mg; 1-nqoH = 500 mg; pH = 5.0 - 5.5.

Table 5.3 Dependence of formation of the precipitate on amount of the reagent [a]

Reagents			Amount of metal in the filtrate		Precipitate[b]	% extracted	
Rh(III) (mg)	Ir(III) (mg)	1-nqoH (mg)	Rh(III) (mg)	Ir(III) (mg)	(mg)	Rh	Ir
50	50	102	144	47.8	147	71.2	4.2
50	50	152	10.6	48.8	158	78.8	3.1
50	50	200	8.4	46.8	216	83.2	6.4
50	50	300	6.9	44.1	242	86.2	13.4
50	50	404	3.6	45.1	305	92.8	9.8
50	50	500	0.9	42.5	400	98.2	15.0

a = pH 5.0 - 5.4; reflux for 90 mins.
b = crude $Rh(1\text{-nqo})_3$

1-oxime the red colour became browner and the volume of the precipitate increased slightly when the amount of reagent was increased. This suggests that at lower concentrations complete precipitation was not obtained. When the quantity of reagent was increased and the mixture refluxed continuously over 1.5 h and left to cool, the precipitation were almost complete. A practically complete precipitation of 50mg of rhodium(III) requires 500mg of the ligand. However, a large excess of reagent begins to cause small amounts of iridium to come out of the solution. When 500mg ligand is used, 98% of rhodium is separated but 15% of iridium is also precipitated.

5.3.3 Effect of pH

The correlation between pH and the amount of precipitation of rhodium is shown in Table 5.4. The studies aimed at establishing the effect of pH were carried out using the optimum heating time and reagent values as determined above. It is evident from Table 5.4 that when the acidity was within the limit of pH 4-6, complete precipitation was observed. It can be seen that in a highly acidic or alkaline medium very little rhodium is precipitated.

The need to recover the ligand can be emphasised by the cost of the compound (100g = £45.90). Thus using 1:10 ratio of metal:ligand, the amount required for 50g of rhodium:500g is £45.90.

Table 5.4. The effect of the reaction medium on the precipitation of rhodium (II) complex[a]

		Amount of metal in the filtrate		% Extracted	
	pH	Rh(mg)	Ir(mg)	Rh	Ir
Acidic[b]	<3	21.7	29.2	27.3	2.6
pH 5.0-6.0		1.2	28.3	96.0	5.7
Alkali[c]	>8	18.0	28.0	40.0	6.6

a = Weight of starting materials
Rh = 30 mg; Ir = 30 mg; 1-nqoh = 300 mg; heating time 2h.

5.4 Extraction of $Rh(1\text{-nqo})_3$ with organic solvents

The first stage of the separation process where rhodium is separated from iridium was achieved successfully. It was decided to develop a new scheme for the refining of rhodium based essentially upon liquid-liquid extraction techniques. This could have the advantages of: i) separations may become quantitative using countercurrent extraction, ii) extractant can be recycled, iii) a more continuous process becomes possible, which in turn reduces labour cost and iv) secondary purification steps may no longer be necessary. When considering extraction systems in large scale production, several factors such as health and fire hazards, cost of solvents, and loss by volatisation and solubility, must be taken into account. Thus, the use of common solvents, e.g. chloroform, carbon tetrachloride, benzene, ether, is very limited generally. High molecular weight aliphatic or aromatic hydrocarbons are often utilised. The extraction of the chelate compound obtained in this study was attempted by adding organic solvents of this type.

Two types of solvents were investigated for the extraction of rhodium. Only trace amounts of rhodium were extracted into the aliphatic Shellsol solvent. However, extraction was partially achieved into Esso Solvesso 200 (an aromatic hydrocarbon mixture) after several days of stirring at room temperature. The solubility of the product was approximately 2-2.5g/litre.

5.5 Recovery of Rhodium from the organic phase

As in gold extraction, in which the gold is deposited as fine sand by reduction with oxalic acid, an attempt was made at generating metallic rhodium by a similar technique (i.e. to combine the strip stage with metal reduction step in one operation). However, there was no evidence of the reduction of rhodium(III) to the metallic form. An alternative method was devised whereby the rhodium complex was treated directly with sodium sulphide. A flow diagram as shown in Figure 5.5 is a new scheme for developing this method.

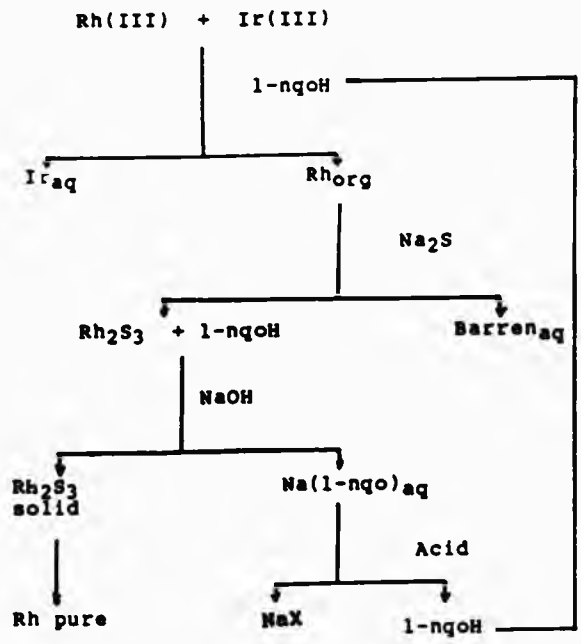

Figure 5.5

Proposed scheme for recovering rhodium.

When the rhodium complex was treated directly with sodium sulphide solution (1%) and the mixture heated for 5 hours, a black residue was obtained and the filtrate afforded a dark brown colour. The black solid was found to be insoluble in all organic solvents, acids, and alkalis. It gave an ill-defined i.r. spectrum. The dark brown filtrate on acidification with $HCl:H_2O(1:1)$ precipitated a dark brown solid which appeared grey when dried. This solid was also insoluble in organic solvents (e.g. methanol, ethanol, acetone, dichloromethane) and water, acid, and alkali and also gave an ill-defined i.r. spectrum. Ignition of the two solids suggested they were of high rhodium content. Ether extraction of the filtrate gave a dark green solid which did not correspond to 1,2-naphthoquinone 1-oxime.

Two methods were utilised for the recovery of rhodium. The black Rh_2S_3 was first treated with 5% sodium hydroxide, so that any nqo^- anion generated forms the sodium salt which can be subsequently extracted. The solid obtained after filtration was ignited to 700°C in a furnace for 1 hour. After all the organic matter was decomposed, the residue, Rh_2O_3, was reduced in a hydrogen atmosphere to produce 99.2% pure rhodium powder. The result of the analysis is presented in Table 5.7. The second method attempted involved digesting the complex Rh_2O_3 in $HCl:H_2O(1:1)$ for 2 days in the presence of chlorine gas. The rhodium dissolved to give a rose coloured solution, suggesting formation of rhodium(III) chloride. Ether extraction of the solution gave a yellow

solid on drying. Tlc showed this to be multicomponent with trace amounts of 1-nqoH present. The rhodium was then recovered by boiling with formic acid to precipitate rhodium which was then ignited and reduced in the presence of hydrogen. The results of the analysis is presented in Table 5.8. Figure 5.6 shows a flow scheme for the whole operation. The second method is an improvement on the first, as the purity is increased.

5.6 Conclusion

The separation of rhodium from iridium was readily achieved by precipitation with 1,2-naphthoquinone 1-oxime. The iridium content as shown in Table 5.7 and Table 5.8 is quite acceptable. However, further purification of the rhodium in order to remove other metals is required. Probably existing processes would have achieved this if applied to $RhCl_3(aq)$ shown in Figure 5.6.

In order to produce viable processes the following problems would have to be addressed:

i) recycling very expensive 1-nqoH

ii) producing pure iridium from aqueous filtrate.

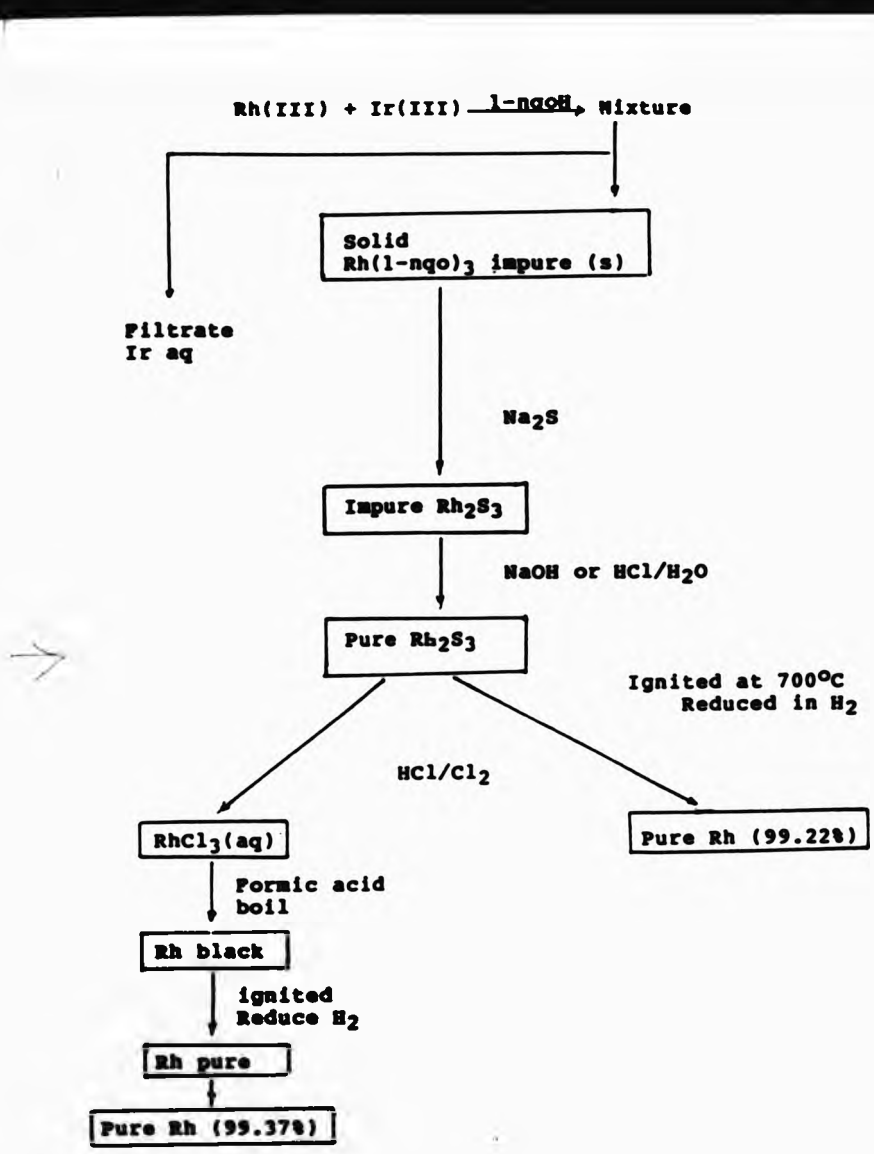
Rh(III) + Ir(III) 1-nqoH Mixture
Solid
Rh(1-nqo)3 impure (s)
Filtrate
Ir aq
Na2S
Impure Rh2S3
NaOH or HCl/H2O
Pure Rh2S3
Ignited at 700°C
Reduced in H2
HCl/Cl2
RhCl3(aq)
Pure Rh (99.22%)
Formic acid
boil
Rh black
ignited
Reduce H2
Rh pure
Pure Rh (99.37%)

Figure 5.6

Table 5.7 Result of analysis of purity of rhodium

Pt	<100 ppm
Pd	10
Ru	<300
Ir	300
Au	30
Ag	2000
Os	<100
Ca	2000
Fe	>1000
Cu	500
Ni	200
Zn	30
Pb	200
Cr	<10
Mn	200
Al	300
Mg	500
Sn	<5
Sb	<10
Bi	200
B	100
Co	<5
Si	200
Na	Strong

Rhodium (by Difference) <99.22%

Table 5.8 Result of analysis of purity of rhodium

Pt	250 ppm
Pd	50
Ru	>1000
Ir	<300
Au	<10
Ag	78
Os	<100
Ca	75
Fe	1000
Cu	60
Ni	500
Zn	50
Pb	200
Cr	400
Mn	40
Al	30
Mg	<10
Sn	750
Sb	400
Bi	3
B	350
Co	75
Si	900

Rhodium (by Difference) <99.37%

5.7 References

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CHAPTER SIX

CATALYTIC OXIDATION

6.1 Introduction

In recent years the synthetic potential of metal complexes derived from quinone mono-oximes has been recognised. These complexes can react with many types of reagents to yield a variety of products, for instance the cycloaddition of the dimethylacetelylene dicarboxylate (DMAD) across the heterodiene system of the quinoneoximato ligand of the $Cu(1\text{-nqo})_2(H_2O)$, $Cu(2\text{-nqo})_2(H_2O)$, $Cu(5\text{-MeOqo})_2$, H_2O complexes to yield benzoxazine (Figure 6.1).[1,2]

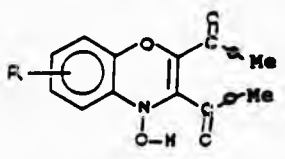
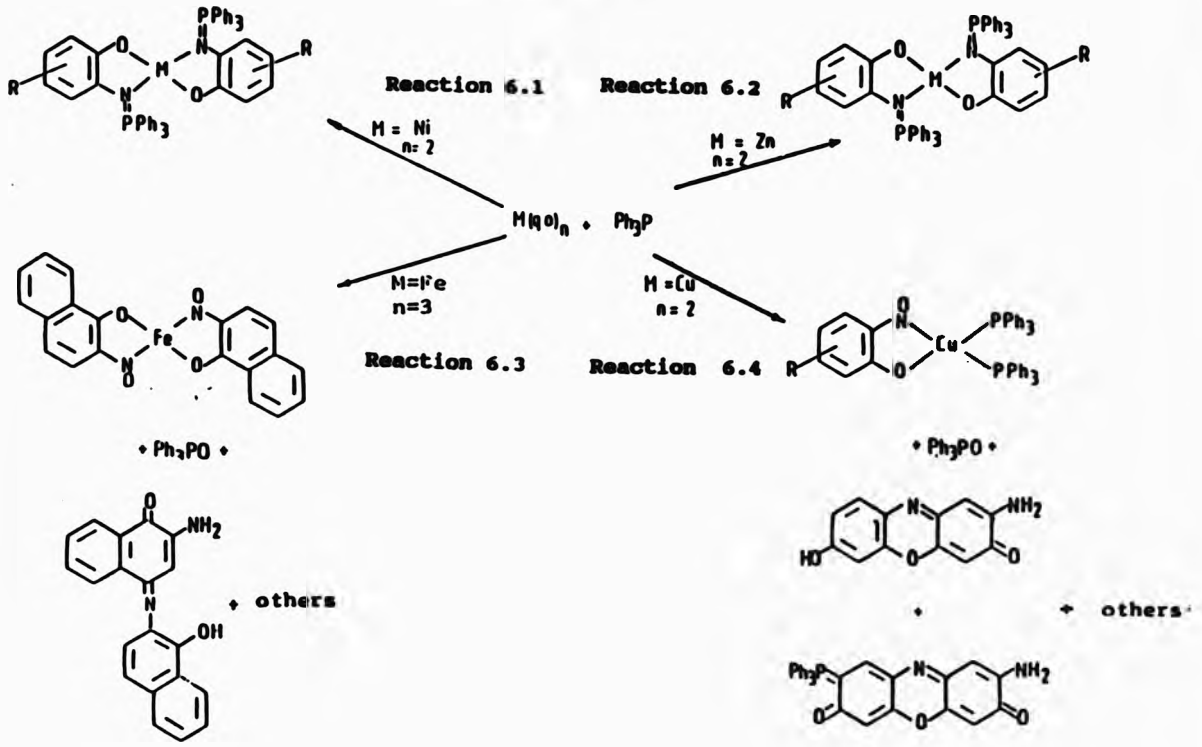


Figure 6.1

Another mode of behaviour of the complexes involves their reactions with Lewis bases. These reactions may lead to adduct formation (Reaction 6.1 and Reaction 6.2 in Scheme 6.1) or give rise to internal redox reaction (Reaction 6.3 and Reaction 6.4 in Scheme 6.1). Internal redox reactions, otherwise referred to as electron transfer reactions or charge transfer reactions, can also be induced by photochemical or thermal means.

Scheme 6.1


Reaction 6.1
Reaction 6.2
M = Ni
n= 2
M = Zn
n= 2
M(NO)n + Ph3P
M=Fe
n=3
M =Cu
n= 2
Reaction 6.3
Reaction 6.4
+ Ph3PO +
+ others
+ Ph3PO +
+ others

Several metal complexes of quinone mono-oximes have shown considerable potential as catalysts for the aerobic oxidation of various types of organic compounds.

1,2-quinone mono-oximato metal complexes have been shown to have novel catalytic properties for the aerobic oxidation of amines.[4] The oxidation of primary aryl-alkylamines to imine is of synthetic importance as there is a dearth of good methods, particularly in non-polar solvents, for amine to imine conversion. The catalytic oxidative transformation of dibenzylamine to N-benzylidenebenzylamine by quinone mono-oximato complexes is of interest, as there are only a limited number of reactions of this type reported in the literature. Also of importance is the low cost and the ease of preparation of the 1,2-quinone mono-oximato complexes compared to other catalysts that have been employed for the oxidation of amines. The catalytic oxidation of amines by 1,2-quinone mono-oximato complexes does not involve the use of alternative oxygen sources such as hydroperoxides. The nature of the amine oxidation product is independent of the reactions conditions employed. The oxidation occurs using mild conditions, i.e., low temperature and atmospheric pressure.

A successful application of the complexes $M_n(nqo)_n$ (n=2 or 3)[5] and $Ru(nqo)_2$[6] as catalysts for the aerobic epoxidation of olefin has been reported. Aerobic oxidation of methyl oleate gave epoxymethyl oleate, as well as acidic and other products. The corresponding oxidation reactions of styrene, cyclohexene, or 1-octene

led to the respective epoxide as the main product.

The use of complexes derived from 1,2-naphthoquinone mono-oximes and involving transition metals such as iron, manganese and chromium, as catalysts for alkene oxidations is advantageous. In addition to the ability of the metal to activate dioxygen, the co-ordinated ligands in such complexes have quinoid and oximic features which can expediate catalytic oxidation. Furthermore, 1,2-naphthoquinone mono-oximato complexes are cheaper than metal porphyrin complexes which are the commonly used catalysts for such oxidations.

The reaction of $Fe(nqo)_3$ (nqo = a mono-oxime of 1,2-naphthoquinone) complexes towards CO have been successfully utilised in the selective filtration of tobacco smoke.[7] Both $Fe(1\text{-}nqo)_3$ and $Fe(2\text{-}nqo)_3$ were shown to be capable of significantly reducing the level of CO in tobacco smoke when supported on suitable filters. This behaviour which is believed to be catalytic and involve dioxygen activation has been patented.[8]

6.2 Oxidation of phenols and catechols

The remarkable ability of certain oxygenases to catalyse oxidative carbon-carbon bond cleavage of various aromatic substrates, most notably of phenols and catechols, is well known. This has lead to intense studies of how living organisms circumvent the low kinetic reactivity of molecular oxygen in reactions with organic substrates.

Oxidative cleavage reactions of aromatic rings is of widespread occurrence in nature and is one of the most important reactions catalysed by dioxygenases. Typically, the enzyme pyrocatechase catalyses the oxidative cleavage of the aromatic ring of catechol by inserting the atoms of molecular oxygen into the substrate. Pyrocatechase and other related oxygenases are known to require the presence of iron or copper for maximum activity. The mechanism proposed for the iron enzyme system involves the direct reaction of catechol with oxygen activated by co-ordination to the iron complex.

Two types of mechanism have been proposed for the pyrocatechase reaction. The first includes the formation of the dioxetan intermediate[9] (Figure 6.2) and the second involves a pathway via an anhydride, the Hamilton intermediate[10] (Figure 6.3) which is more thermodynamically favourable than the dioxetan.

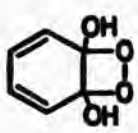


Figure 6.2

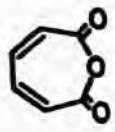


Figure 6.3

While the precise mechanism of these transformations remains uncertain, it is becoming increasingly clear that molecular oxygen is not involved directly in reactions

with these substrates. It has been generally accepted that the required activation of molecular oxygen in enzyme systems is achieved by the reaction of the oxygen with the transition metal bonded to the enzyme molecule. It is then the reaction of these oxygen-containing intermediates with the complex organic substrate that brings about the observed oxidation reaction.

The possible role of superoxide ion in certain biological oxidations is well recognised and the investigations of superoxide ion chemistry in vitro[11-16] as a model for the oxidative carbon-carbon bond cleavage of catalysed by pyrocatechase and metapyrocatechase has already been carried out.[17,18]

Several non-enzymic model reactions have been investigated but few reactions are known which can be considered to be analogous to enzymic reactions. Table 6.1 shows some examples of catalytic oxidation of phenols. The total insertion of molecular oxygen has been accomplished in several reactions. However, the catalytic activity of complexes has been very low.

An example of the catalytic cleavage of 3,5-di-tert-butylcatechol by an iron(II) complex has been reported.[19] The oxidative aromatic opening was achieved by insertion of molecular oxygen, with O-O bond cleavage, to form the lactone(I) (Reaction 6.5). The active complex and the reaction mechanism are not clear.

Table 6.1 Some reported catalytic oxidation reactions of phenols

Complex	Phenol	Products (%)	Ref
$VO(acac)_2$	DTBC	a(41) b(15) c(27)	20
$VCl(Salen)_2$	DTBC	a(43) b(7) c(28)	20
Co(Salen)	DTBC	a(39) b(7) c(22)	21
VO(Saldpt)	DTBC	a(41) b(6) c(23)	20
$RuCl_2(PPh_3)_3$	DTBC	a(26) b(64) d(16)	22
Fe(II)Bpy	DTBC	c(18-51) d(0-14)	23
$Fe(bpnp)Cl_2$	DTBC	a(10) b(40)	23
Fe(Salen)	DTBC	b(70)	21
$K_4[Fe(CN)_6]$	DBMP	e(66) f(34)	24
Co(Salpn)	DBP	g(52) h(48)	25
$Co(dmgH)_2py$	DBP	g(100)	25
Mn(tpp)Cl	DBP	g(40) h(60)	25

a = Muconic acid anhydride

b = Benzoquinone

c = 2H-pyran-2-one

d = Furanone

e = 2,6-Di-tert-butyl-4-(methoxymethyl)-phenol

f = 2,6-Di-tert-butyl-4-methyl-4-methoxy-cyclohexa-2,5-dienone

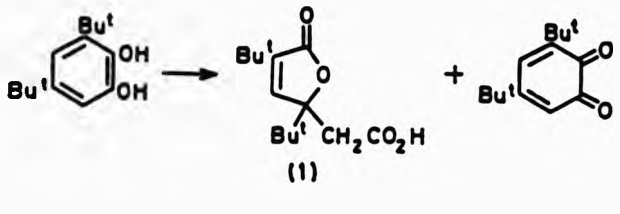
g = 2,6-di-tert-butyl-p-benzoquinone

h = Diphenoquinone

DTBC = 3,5-Di-tert-butylcatechol

DMBP = 2,6-Di-tert-butyl-4-methylphenol

DBP = 2,6-Di-tert-butylphenol

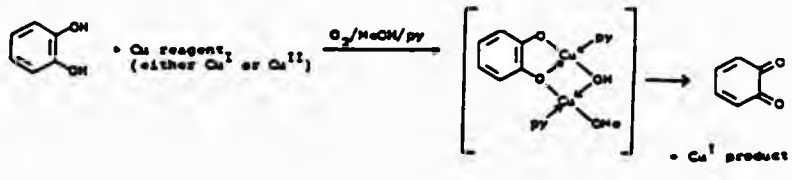


(1)

(Reaction 6.5)

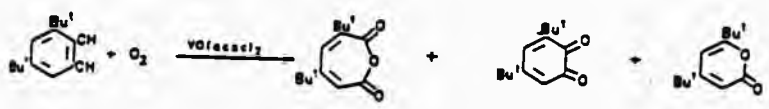
In model reactions using copper(I) catalyst, in the presence of pyridine and methanol for the oxygenation of catechols, gives muconic acid monoethyl ester as the main product.[26] The actual species responsible for the oxygenation is copper(II) complex (Reaction 6.6).

The activation of molecular oxygen in metal complex catalysed systems is achieved by the reaction of oxygen with the transition metal. Although these systems are extremely complex, it has been established that the initial state of oxygenation involves complex formation between the catechol and the active copper(II) species. In the reaction that follows, copper(II) is reduced to copper(I) and benzoquinone is produced during a step which involves an internal redox reaction. The benzoquinone then reacts further with one or more of the copper species present to give rise to *cis,cis* muconic acid monoethyl ester.



(Reaction 6.6)

Several vanadium(III) complexes efficiently catalyse the oxygenation of 3,5-di-tert-butyl catechol to 3,5-di-tert-butylmuconic acid anhydride and 4,6-di-tert-butyl-1,2-pyrone[20] (Reaction 6.7).



(Reaction 6.7)

The muconic acid anhydride was the main product found in this reaction, indicating that the vanadium complex catalysed intradiol cleavage of the catechol.

6.3 A study of the oxidation of catechols using nitroso-R-salt complexes of iron or copper as catalysts

In this study, the potential aerobic oxidation of 3,5-di-tert-butylcatechol, 4-tert-butylcatechol and catechol, using 1,2-naphthoquinone 1-oximato-3,6-disulphonic acid metal complexes was examined. These were selected as substrate, as they represent a range of

reactivities with regard to aerobic oxidation. Furthermore, these phenols have been used as substrates by other workers and therefore yields and turnover numbers can be compared.

All oxidation reactions were carried out at room temperature and/or at 70°C, under oxygen and in air. Reaction progress was monitored using glc and tlc techniques. The products were characterised by mass spectrometry and ir spectroscopy. The effect of time, solvent, aeration and amount of catalyst was also investigated.

Oxidation of 3,5-di-tert-butylcatechol

The results of the oxidation reaction of 3,5-di-tert-butylcatechol using iron(II) or copper(II) complex of 1,2-naphthoquinone 1-oximato-3,6-disulphonic acid are summarised in Table 6.2.

When the 3,5-di-tert-butylcatechol (20 mmol) and Fe(nRsHNa) (0.20 mmol) was stirred in aqueous methanol at room temperature under oxygen, muconic acid anhydride, 2H-pyran-2-one and benzoquinone were obtained in yield of 34,16,21% respectively. Some unreacted catechol was recovered (21%). The total conversion of oxidation product was 79%. Catalyst decomposition was not observed and the catalyst was recovered in near quantitative yield.

The catalytic activity of the copper complex, Cu(nRsHNa), was slightly lower than that of iron complex, but the products were muconic acid anhydride (17%),

Table 6.2 Aerobic oxidation of 3,5-di-tert-butylcatechol catalysed by complexes of nitroso-R-salt[a]

Complex	Conditions	Yield of Products (%)[g]				Conversion %
		1	2	3	4	
Fe(nRsHNa)	b	34	16	21	-	79
Fe(nRsHNa)	c	37	20	25	-	82
Fe(nRsHNa)	d	NR	NR	NR	-	-
Fe(nRsHNa)	e	26	11	13		50
Fe(nRsHNa)	f	18	8	13		39
Cu(nRsHNa)	b	17	-	26	8	42
Cu(nRsHNa)	c	20	-	27	13	60
Cu(nRsHNa)	d	NR	NR	NR	NR	-
Cu(nRsHNa)	e	11	-	18	9	38
Cu(nRsHNa)	f	13	-	16	9	38

a = Initial concentration of 3,5-di-tert-butylcatechol (DTBC) = 20 mmol.

b = Oxygen atmosphere/room temperature/200h in methanol

c = Oxygen atmosphere/room temperature/200h in pyridine/methanol

d = Oxygen atmosphere/room temperature/200h in excess pyridine

e = Oxygen atmosphere/room temperature/200h in toluene

f = Oxygen atmosphere/room temperature/200h in tetrahydrofuran

g = Yield based on DTBC.

1 = Muconic acid anhydride

2 = 2H-pyran-2-one

3 = Benzoquinone

4 = Acidic component

benzoquinone (26%) and an unidentified acid compound (18%). When $Ni(nRsNa)_2$ or $Rh(nRsNa)_3$ were used, no oxidation of the substrate occurred, even at 70°C.

The systems metal complex-catechol were also studied using tetrahydrofuran, toluene or acetonitrile as solvents. In these cases the products were obtained in low yield. When the reactions were carried out in air, no oxidation of the substrate occurred even at 70°C.

Previously it has been reported that the addition of pyridine, or substituted pyridines, greatly affects the reactivity and selectivity of the products. For example, oxygenation of 3,5-di-tert-butylcatechol by various vanadyl complexes is completely inhibited in the presence of pyridine. On the other hand, pyridine is essential for the formation of furanone from the catechol when iron(II) complexes are used as catalysts. However, the use of 1,10-phenanthroline or ethylamine in place of bipyridine retards such reactions.

The presence of pyridine in the catalytic oxidation of alkenes by 1,2-quinone mono-oxime complexes has been reported to increase the rate of reaction. This has been attributed to the co-ordination of pyridine by electron donation to form a high-valent oxo-metal intermediate. This 'pyridine effect' was observed in the catalyst systems involving the complexes $Mn(nqo)_2$,[5] $Mn(nqo)_3$[5] and $Ru(nqo)_2$.[6]

When the oxidation of 3,5-di-tert-butylcatechol in methanol using iron(II) as catalyst was carried out in the presence of a small amount of pyridine an increase in the rate of reaction was observed, relative to the

corresponding reaction in the absence of pyridine, but the nature and yield of products was not altered. Similar behaviour was observed for the oxidation of 3,5-di-tert-butylcatechol using Cu(II) as catalyst in the presence of a small amount of pyridine. In marked contrast, when the reactions were carried out in larger amounts of pyridine the oxidation was completely suppressed. This is probably due to the limited solubility of the complex in pyridine.

The results of the oxidation of 3,5-di-tert-butylcatechol investigated under different conditions and using the complexes Fe(II) and Cu(II) as catalysts are summarised in Table 6.3. The yields of product and the lack of reaction in the absence of the complexes under the condition suggest catalytic behaviour. The results also indicate that increase in catalyst concentration shortens the reaction time but is not effective in increasing the yield. This may be due to the low solubility of the complexes and the occurrence of side reactions such as the polymerisation of 3,5-di-tert-butylcatechol.

Oxidation of 4-tert-butylcatechol

When 4-tert-butylcatechol (20 mmol) and Fe(nRs Na) (0.20 mmol) were stirred in aqueous methanol at room temperature under an atmosphere of oxygen, muconic acid anhydride (10%) benzoquinone (23%) and 2H-pyran-2-one product (8%) were obtained. Repeating the experiment using methanol and some pyridine the rate of reaction was

Table 6.3 Catalytic oxidation of 3,5-di-tert-butylcatechol by nitroso-R-salt complex

Complex	Amount of catalyst (mmol)	Yield of products (%)[b]			
		1	2	3	4
Fe(nRs Na)	0.10	30	16	18	
	0.20	33	15	23	
	0.30	36	18	25	
	0.40	39	17	21	
	0.50	39	19	26	
	1.00	40	23	24	
	2.00	40	21	28	2
Cu(nRs Na)	0.10	16	-	24	8
	0.50	19	-	28	10
	1.00	20	-	27	14

a = Reaction conditions: concentration of pyrocatechol (20 mmol) in aq-methanol; 200h; 1 atm. O_2 at room temperature.

b = Yield of products is based on pyrocatechol.

c = The solution was inhomogenous, containing undissolved complex.

1 = Muconic acid anhydride

2 = 2H-pyran-2-one

3 = Benzoquinone

4 = Unidentified acid product

increased and the yield of the products improved slightly. Using Cu(nRs:Na) the results were similar but yields slightly lower (Table 6.4).

Oxidation of Catechol

From the oxidation reaction between catechol(20 mmol) and catalyst(0.20 mmol) in aqueous methanol at room temperature under an atmosphere of oxygen, benzoquinone was obtained as the main product in yield of up to 25%. Production of small amounts of muconic acid anhydride and other acid product was also observed. Again, addition of a small amount of pyridine to the solvent leads to a slight increase in the rate of reaction (Table 6.4).

6.4 Mechanistic aspects of oxidation reactions

In order to assess the mechanism of the catalytic oxidation of 3,5-di-tert-butylcatechol using Fe(nRs Na) or Cu(nRs Na) as catalysts, the formation of products as a function of time was investigated. In addition the reactions were investigated in the presence of small amounts of pyridine. G.l.c. analysis was utilised to monitor the reactions and reaction profiles were plotted for the reactions.

The reaction profiles indicated that the iron catalysed reactions differ from the corresponding copper system (Figure 6.4 and Figure 6.5). In the case of the iron system, benzoquinone increases and then slightly decreases. Concurrent with the decrease of benzoquinone

Table 6.4 Aerobic oxidation of catechol by complexes of nitroso-R-salt complex

Complex	Catechol	Yield of Products (%)[g]			
		1	2	3	4
Fe(nRs Na)	TBC[d]	23	10	8	
Fe(nRs Na)	TBC[d]	25	13	9	
Cu(nRs Na)	TBC[d]	18	9	-	7
Cu(nRs Na)	TBC[d]	23	12	-	9
Fe(nRs Na)	Catechol	19	10	6	
Fe(nRs Na)	Catechol	22	11	8	
Cu(nRs Na)	Catechol	17	10		7
Cu(nRs Na)	Catechol	19	12	-	9

a = Initial concentration of the catechol = 20 mmol and catalyst = 0.20 mmol.

b = Oxygen atmosphere/room temperature/120h in methanol.

c = Oxygen atmosphere/room temperature/120h in pyridine.

d = 4-tert-butylcatechol.

e = Yields based on the substrate.

1 = Benzoquinone
2 = Muconic acid anhydride
3 = 2H-Pyran-2-one
4 = Acidic component

Figure 6.4 Reaction profile for the oxidation of 3,5-di-tert-butylcatechol catalysed by Fe(nRs Na).H_2O at 20°C

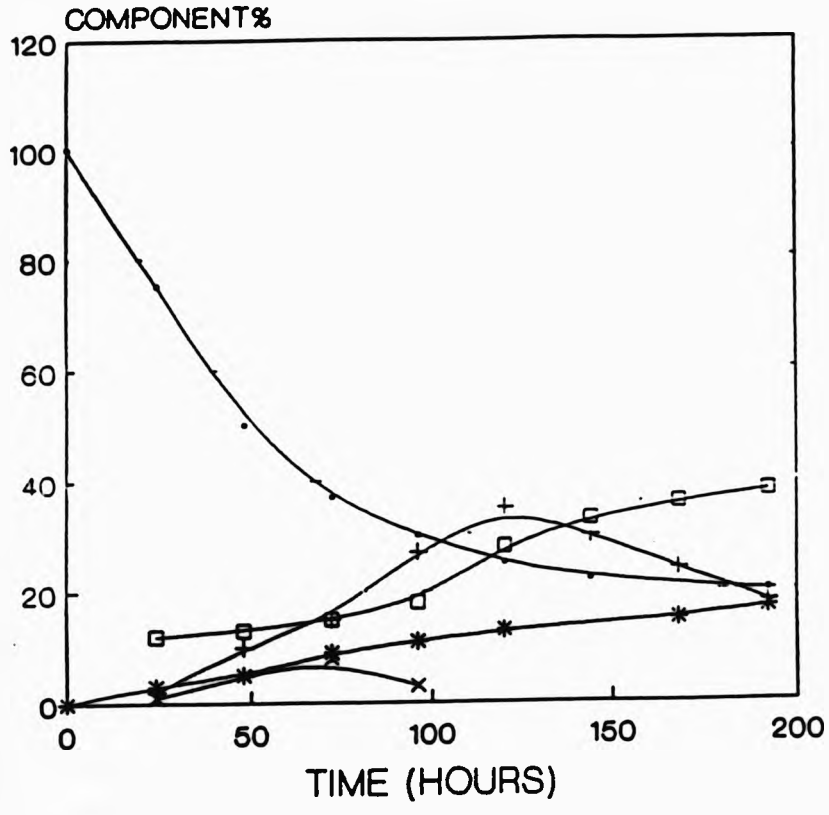
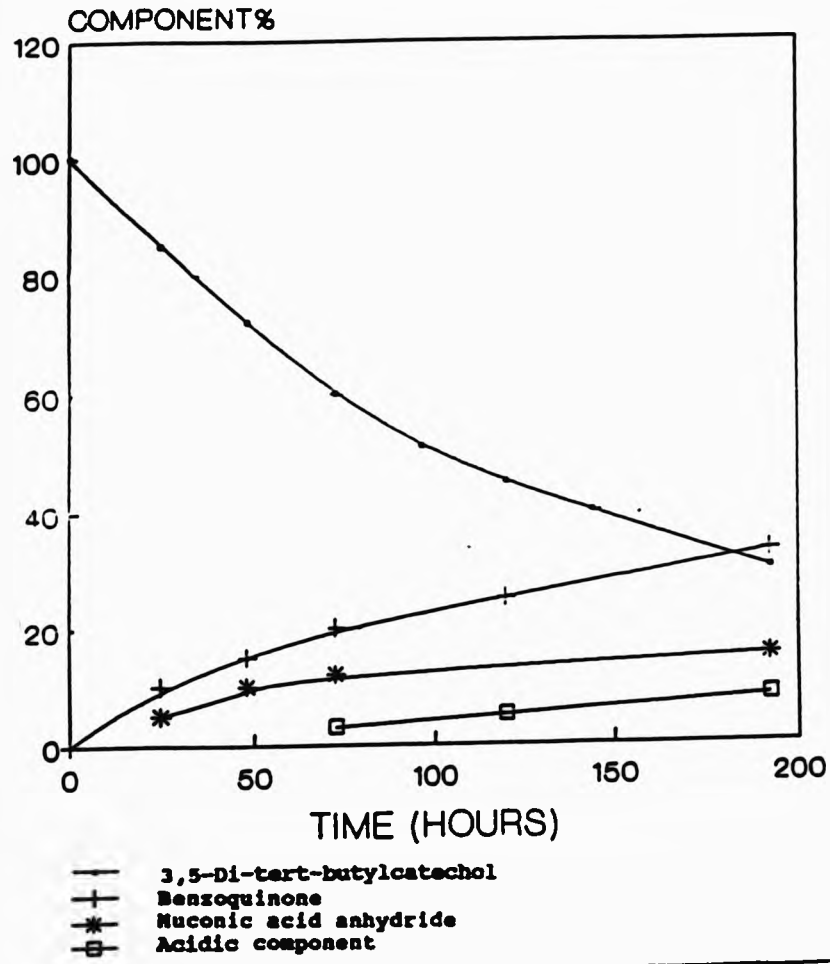


Figure 6.5 Reaction profile for the oxidation of 3,5-di-tert-butylcatechol catalysed by Cu(nRs Na) at 20°C



there is an increase in the concentration of muconic acid anhydride and 2H-pyran-2-one. Furthermore, two unidentified compounds are formed at an early stage of the reaction and then gradually disappear. In the case of the copper system all these products show gradual increase, although small amounts of products are formed which are not included in the profiles.

When the oxidations were carried out in the presence of small amount of pyridine, there is a slight increase in the rate of oxidation but the overall appearance of the profiles is not affected (Figure 6.6 and Figure 6.7).

Although no definite mechanistic suggestion can be made it appears that the iron catalysed system involves one or more intermediates which ultimately lead to higher yield of muconic acid anhydride and 2H-pyran-2-one. Whereas in the copper catalysed system no intermediates are detected, however, the oxidation gave a mixture of products which contained an acidic component.

It appears that the metal possibly plays a specific role in the formation of the oxygenation products. In previous studies it has been suggested that an active complex is involved in the oxygenation reactions. An attempt to gain some understanding regarding the nature of the intermediate metal complex by measuring electronic spectral changes proved unsuccessful. Furthermore, the complexes recovered had not incurred any changes as indicated by i.r. and t.l.c.

Figure 6.6 Reaction profile for the oxidation of 3,5-di-tert-butylcatechol catalysed by Fe(nRs Na) at 20°C in the presence of pyridine

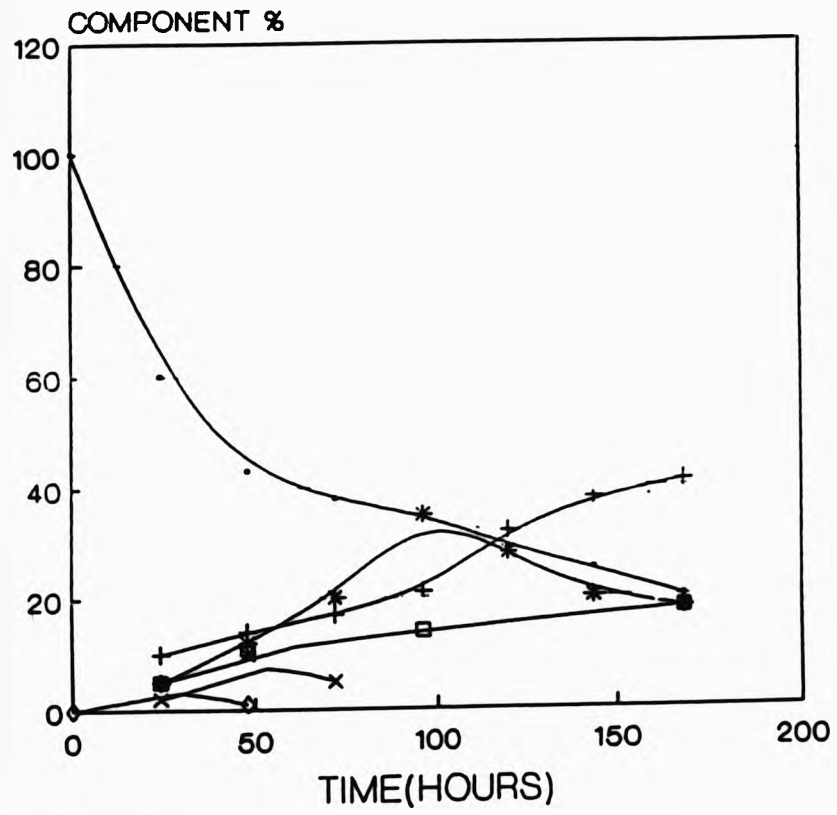
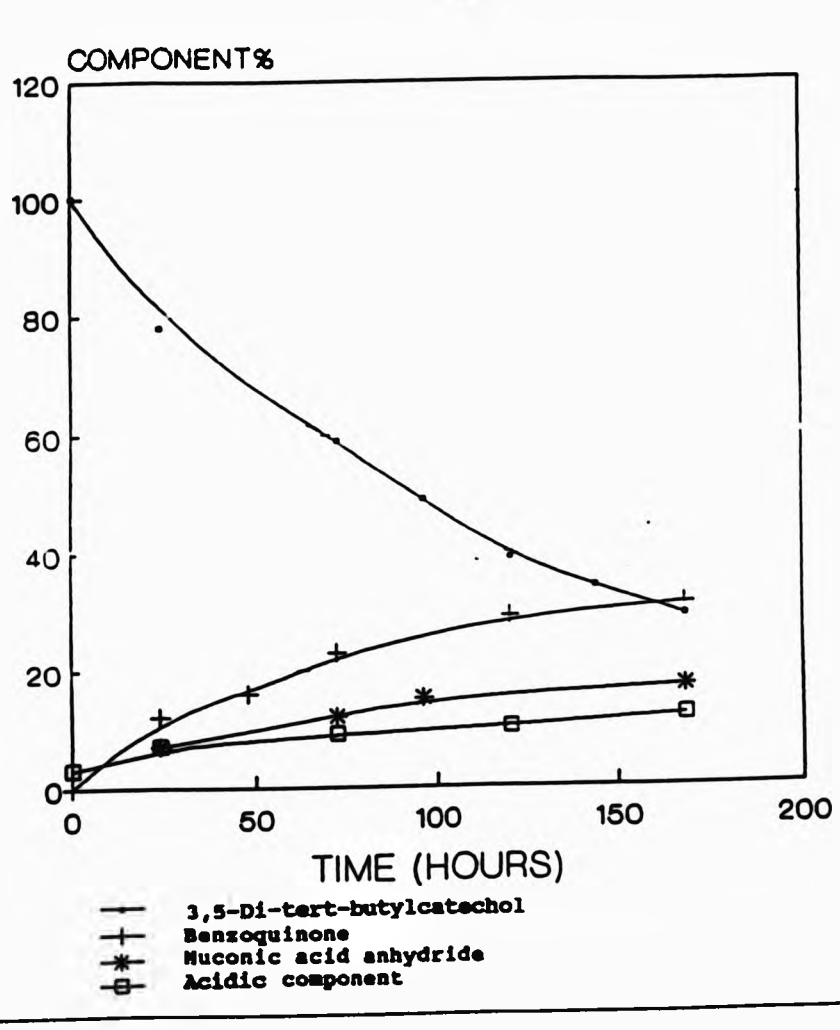


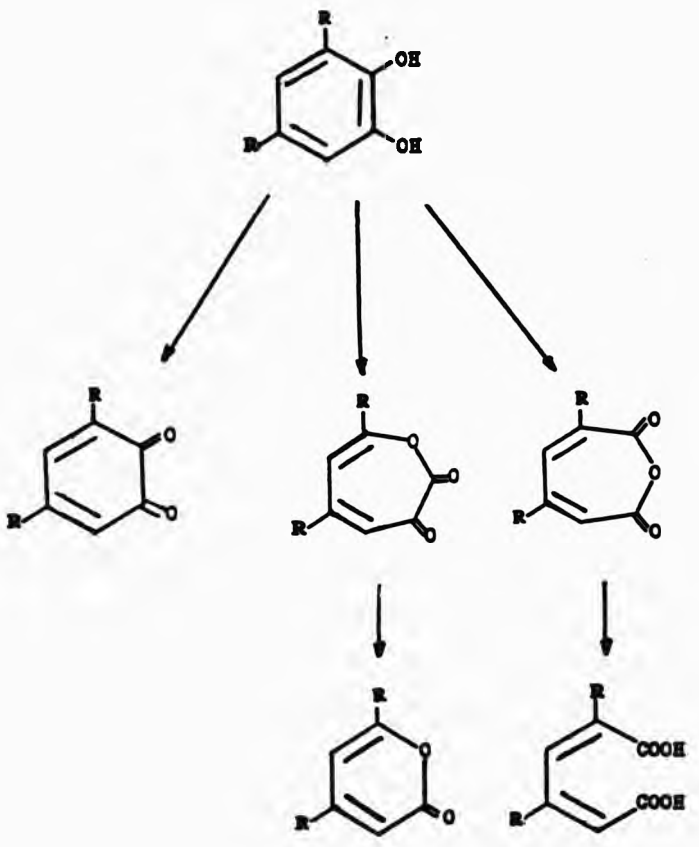
Figure 6.7 Reaction profile for the oxidation of 3,5-di-tert-butylcatechol catalysed by Cu(nRs Na) at 20°C in the presence of pyridine



As one of the products, muconic acid anhydride, is analogous to the Hamilton intermediate in the enzymatic reaction, the iron and copper complexes catalysed oxygenation favours the Hamilton intermediate rather than the dioxetan intermediate in oxidative ring cleavage reactions of the pyrocatechols. This infers that the oxidation of the catechols involves oxidative cleavage of the C-C bond through insertion of molecular oxygen.

The formation of quinone is a common occurrence in these oxygenation reactions. It may undergo further oxidation to give the various products. Consequently, to determine whether the overall reaction of catechols involves quinone as a reaction intermediate, a mixture of the iron(II) complex and the quinone gave small amounts of 2H-pyran-2-one. This suggests that the products were mainly obtained directly from 3,5-di-tert-butylcatechol. Scheme 6.1 shows the possible reaction pathway.

Although few mechanisms have been proposed, none of them seems to be conclusive. The characteristic feature of the oxidation of catechols using iron and copper complexes of nitroso-R-salt is the formation of products of extradiol oxygenation and one of the intermediates supposed in biochemical systems.



Scheme 6.2 Oxidation of 3,5-di-tert-butylcatechol using iron or copper complexes of 1,2-naphthoquinone 1-oxime -3,6-disulphonate complexes.

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CHAPTER SEVEN

EXPERIMENTAL

7.1 General

The reagents and solvents used were generally of GPR grade and were used without further purification. The adsorbent used for column chromatography was Merck Kieselgel 60 (70-230 mesh). Tlc was carried out using precoated Merck Kieselgel $60F_{254}$ plates.

7.2 Analytical Techniques

Carbon, hydrogen and nitrogen analyses were carried out by the microanalytical services at the Polytechnic of North London. Metal analyses were carried out by atomic absorption spectroscopy on a Pye Unicam SP9 machine at the Polytechnic of North London. Wet oxidation was achieved by charring an accurately weighed quantity of sample (ca. 0.20g) with a mixture of concentrated sulphuric acid then boiling in a mixture of concentrated nitric acid (5 cm^3) and 100 volume hydrogen peroxide.

7.3 Physical techniques

Infrared spectra over the region 600-4000 cm^{-1} were recorded on a Perlin-Elmer 5 spectrophotometer. The spectra were recorded as KBr discs. Ultraviolet and visible spectra in the region 200-900 nm were recorded on a Perkin-Elmer Lambda 5 spectrophotometer. An A.E.I. MS9 double focusing spectrometer was used for mass spectrometry.

^{1}H nuclear magnetic resonance were obtained using a Perkin-Elmer R12B 60 MHz spectrometer and at the Polytechnic of North London. Tetramethylsilane was used as the standard reference.

Room temperature magnetic moments were measured using a Gouy balance equipped with a permanent magnet of field strength 3600 oersted. The variable temperature magnetic studies were carried out using a Newport Instruments Gouy balance at field strengths of 3500, 5500, 6400, and 7100 Oersted at intervals over the temperature range 93-295°K. In both cases, the apparatus was calibrated with mercury tetrathio cyanatocobaltate(II). All the magnetic measurements were carried out in duplicate to check on packing errors. The magnetic susceptibility values were corrected for diamagnetism.

7.4 Reactions

7.4.1 Reaction of hydrated rhodium(III) chloride with 1,2-naphthoquinone mono-oxime in methanol

A solution of hydrated rhodium(III) chloride (2.09g; 7.9 mmol) in water (50 cm^3) was added to a solution of 1,2-naphthoquinone 1-oxime (5.21g; 30.1 mmol) in methanol (100 cm^3) and the mixture was stirred under reflux for 72h. Filtration gave a solid which was washed with water. The solid was separated by extraction technique as shown in Scheme 2.1 (Chapter 2). This gave a mixture of isomer of tris(1,2-naphthoquinone 1-oximato) rhodium(III) (2.10g; 41%) (Found: C, 57.9; H, 3.4; N, 6.4; Rh, 16.1%. $C_{30}H_{18}N_3O_6Rh$ requires: C, 58.2;

H, 2.9; N, 6.8; Rh, 16.6%) and a second solid (multicomponent by tlc) (0.62g).

Similarly, reaction of hydrated rhodium(III) chloride (2.00g, 7.8 mmol) with 1,2-naphthoquinone 2-oxime (5.20g, 30.0 mmol) afforded a mixture of isomers of tris(1,2-naphthoquinone 2-oximato) rhodium(III) (2.00g, 40%). (Found: C, 58.7; H, 3.1; N, 6.9; Rh, 16.7%. $C_{30}H_{18}N_3O_6Rh$ requires: C, 58.2; H, 2.9; N, 6.8; Rh, 16.6%).

7.4.2 Reaction of hydrated rhodium(III) chloride with 1,2-naphthoquinone mono-oxime in aqueous methanol

A solution of hydrated rhodium(III) chloride (2.01g, 7.8 mmol) in water (50 cm^3) was added to a solution of 1,2-naphthoquinone 1-oxime (5.21g; 30.1 mmol) in 2:1 methanol (100 cm^3) and the mixture was stirred under reflux for 1h. Separation achieved as above gave a mixture of isomers of tris(1,2-naphthoquinone 1-oximato) rhodium(III) (2.41g; 48%). (Found: C, 58.1; H, 3.3; N, 6.1: Rh, 16.1%. $C_{30}H_{18}N_3O_6Rh$ requires: C, 58.2; H, 2.9; N, 6.8; Rh, 16.6%).

Similarly, reaction of hydrated rhodium(III) chloride (2.01g; 7.8 mmol) with 1,2-naphthoquinone 2-oxime (5.20g; 30.0 mmol) afforded a mixture of isomers of tris(1,2-naphthoquinone 2-oximato) rhodium(III) (2.30g; 47%). (Found: C, 59.0; H, 3.2; N, 6.9; Rh, 16.8%. $C_{30}H_{18}N_3O_6Rh$ requires: C, 58.2; H, 2.9; N, 6.8; Rh, 16.6%).

7.4.3 Reaction of hydrated rhodium(III) chloride with 1,2-naphthoquinone mono-oxime or its sodium salt in the presence of a sodium acetate/acetic acid buffer

A solution of hydrated rhodium(III) chloride (2.09g; 7.9 mmol) in water (50 cm^3) was added to a solution of 1,2-naphthoquinone 1-oxime (5.24g; 30.3 mmol) in acetone (100 cm^3) in a sodium acetate-acetic acid buffered medium at pH 5-6, and the mixture was heated under reflux for 2h. Filtration gave a solid which was washed with water, dried at 60°C/30mmHg and chromatographed. Elution with toluene gave a mixture of purple isomers of tris(1,2-naphthoquinone 1-oximato) rhodium(III) (3.25g; 67%) (Found: C, 57.8; H, 3.4; N, 6.2; Rh, 16.0%. $C_{30}H_{18}N_3O_6Rh$ requires: C, 58.2; H, 2.9; N, 6.8; Rh, 16.6%)

Similarly, hydrated rhodium(III) chloride (2.00g; 7.6 mmol) in water (50cm^3) was added to a solution of the 1,2-naphthoquinone 2-oxime (5.29g; 30.8 mmol) in acetone (100 cm^3) in a sodium acetate-acetic acid buffered medium at pH 5-6 and the mixture was heated under reflux for 2h. Filtration gave a solid which was washed with water, dried at 60°C, and chromatographed on a silica column. Elution with toluene gave a mixture of isomers of tris(1,2-naphthoquinone 2-oximato) rhodium(III) (3.35g; 69%) (Found: C, 59.0; H, 3.2; N, 6.9; Rh, 16.3%. $C_{30}H_{18}N_3O_6Rh$ requires: C, 58.2; H, 2.9; N, 6.8; Rh, 16.6%)

Similarly hydrated rhodium(III) chloride (2.00g; 7.6 mmol) and sodium 1,2-naphthoquinone 2-oximato (5.40g; 27.7 mmol) gave tris(1,2-naphthoquinone 2-oximato)

rhodium(III) (3.15g; 67%) (identified by tlc and ir).

7.4.4 Reaction of chloroiridic(III) acid with 1,2-naphthoquinone mono-oxime in methanol

A solution of chloroiridic(III) acid (4.00 cm^3, containing 0.54g of Ir) was added to a solution of 1,2-naphthoquinone 1-oxime (7.01g; 37.5 mmol) in methanol (100 cm^3) and the mixture was stirred under reflux for 10 days. The mixture was filtered to give a dark brown solid (3.90g), dried at 60°C/30 mm Hg and chromatographed. Elution with toluene gave a mixture of isomer of tris(1,2-naphthoquinone 1-oximato) iridium(III) (0.36g; 18%). (Found: C, 49.3; H, 3.7; N, 5.4; Ir, 26.6%. $C_{30}H_{18}N_3O_6Ir$ requires: C, 50.8; H, 3.3; N, 5.9; Ir, 27.1%).

Similarly, reaction of chloroiridic(III) acid (4.00 cm^3 containing 0.55g of Ir) was added to a solution of 1,2-naphthoquinone 2-oximate (7.00g; 37.5 mmol) in methanol (100 cm^3) gave a mixture of isomer of tris(1,2-naphthoquinone 2-oximato) iridium(III) (0.36g; 18.6%). (Found: C, 48.7; H, 3.9; N, 5.4; Ir, 26.9%. $C_{30}H_{18}N_3O_6Ir$ requires: C, 50.8; H, 3.3; N, 5.9; Ir, 27.1%).

7.4.5 Reaction of chloroiridic(III) acid with 1,2-naphthoquinone mono-oxime in methanol

A solution of chloroiridic(III) acid (4.00 cm^3, containing 0.54g of Ir) was added to a solution of 1,2-naphthoquinone 1-oxime (7.01g; 37.5 mmol) in methanol (100 cm^3) and the mixture was stirred under reflux for 5

days. The mixture was filtered to give a dark brown solid (4.01g), dried at 60°C/30 mm Hg and chromatographed. Elution with toluene gave a mixture of isomer of tris(1,2-naphthoquinone 1-oximato) iridium(III) (0.30g; 17%). (Found: C, 51.0; H, 3.3; N, 5.5; Ir, 26.6%. $C_{30}H_{18}N_3O_6Ir$ requires: C, 50.8; H, 3.3; N, 5.9; Ir, 27.1%).

Similarly, reaction of chloroiridic(III) acid (4.00 cm^3 containing 0.54g of Ir) was added to a solution of 1,2-naphthoquinone 2-oxime (7.00g; 37.5 mmol) in methanol (100 cm^3) gave a mixture of isomers of tris(1,2-naphthoquinone 2-oximato) iridium(III) (0.38g; 19.0%). (Found: C, 50.5; H, 3.5; N, 5.4; Ir, 26.7%. $C_{30}H_{18}N_3O_6Ir$ requires: C, 50.8; H, 3.3; N, 5.9; Ir, 27.1%).

7.4.6 Reaction of chloroiridic(III) acid with 1,2-naphthoquinone mono-oxime or its sodium salt in the presence of a sodium acetate/acetic acid buffer

Chloroiridic(III) acid (4.00 cm^3, containing 0.54g of Ir) was added to a solution of 1,2-naphthoquinone 1-oxime (7.0g; 37.5 mmol) in 1:1 water-accetone (200 cm^3) buffered at pH 4-5 with sodium acetate-acetic acid and heated under reflux for 5 days. The mixture was filtered to give a dark brown solid (4.28g) which was dried at 60°C/30mmHg and chromatographed. Elution with toluene gave tris(1,2-naphthoquinone 1-oximato) iridium(III) (0.41g; 20%) (Found: C, 49.6; H, 3.7; N, 5.4; Ir, 26.7%. $C_{30}H_{18}IrN_3O_6$ requires: C, 50.8; H, 3.3; N, 5.9; Ir, 27.1%).

7.4.7 Reaction of chloroiridic(III) acid with 1,2-naphthoquinone 2-oxime or its sodium salt in the presence of a sodium acetate/acetic acid buffer

Chloroiridic(III) acid (4.00 cm^3, containing 0.54g of Ir) was added to a solution of 1,2-naphthoquinone 2-oxime (7.00g; 37.5 mmol) in 1:1 water-acetone (200 cm^3) buffered at pH 4-5 with sodium acetate-acetic acid and heated under reflux for 5 days. The mixture was filtered to give a dark brown solid (4.28g) which was dried at 60°C/30mmHg and chromatographed. Elution with toluene gave tris(1,2-naphthoquinone 2-oximato) iridium(III) (0.40g; 20%) (Found: C, 49.1; H, 3.5; N, 5.3; Ir, 26.7%. $C_{30}H_{18}IrN_3O_6$ requires: C, 50.8; H, 3.3; N, 5.9; Ir, 27.1%).

Similarly, reaction of sodium 1,2-naphthoquinone 2-oximato (7.00g, 35 mmol) with chloroiridic(III) acid (4.00 cm^3, containing 0.54g of Ir) afforded tris(1,2-naphthoquinone 2-oximato) iridium(III) (0.49g; 21%) (Found C, 49.3; H, 3.1; N, 5.6; I, 26.8%. $C_{30}H_{18}IrN_3O_6$ requires: C, 50.8; H, 3.3; N, 5.9; Ir, 27.1%).

7.4.8 Nitrosation of 1- or 2-naphthol in the presence of hydrated rhodium(III) chloride

a) A solution of sodium nitrite (5.13g; 74.3 mmol) in water (50 cm^3) was added to a stirred solution of 1-naphthol (4.01g; 29.9 mmol), hydrated rhodium(III) chloride (1.98g; 7.5 mmol), acetic acid (10 cm^3) and sodium acetate (10.00g) in 2:1 mixture of methanol and water (300 cm^3). After 20h at room temperature the mixture was filtered to give a dark purple solid

which was washed with water and dried at 60°C/30mmHg. The product was chromatographed on a silica column. Elution was carried out with toluene and gave tris(1,2-naphthoquinone 2-oximato) rhodium(III) (1.90g; 39%) (Found: C, 58.3; H, 2.8; N, 6.5; Rh, 16.7%. $C_{30}H_{18}RhN_3O_6$ requires: C, 58.2; H, 2.9; N, 6.8; Rh, 16.6%).

b) Nitrosation of 2-naphthol (5.00g, 74.3 mmol) in the presence of hydrated rhodium(III) chloride (2.01g; 7.5 mmol) was carried out in a similar way to the nitrosation of 1-naphthol to give wine-red tris(1,2-naphthoquinone 1-oximato) rhodium(III) (1.60g; 32%). (Found: C, 57.9; H, 3.1; N, 6.6; Rh, 16.3%. $C_{30}H_{18}RhN_3O_6$ requires: C, 58.2; H, 2.9; N, 6.8; Rh, 16.6%).

7.4.9 Nitrosation of 1- or 2-naphthol in the presence of chloroiridic(III) acid

A solution of sodium nitrite (4.00g; mmol) in water (50 cm^3) was added to a stirred solution of 1-naphthol (3.00g; 20.8 mmol), chloroiridic(III) acid (3.00 cm^3, containing 0.41g of Ir, 2.2 mmol), acetic (10 cm^3) and sodium acetate (10.00g) in 2:1 methanol-water mixture (300 cm^3). After 6 days at room temperature the reaction gave unreacted 1-naphthol (32%) and 1,2-naphthoquinone (identical tlc, ir with an authentic sample). Tlc of the filtrate indicated a

multicomponent mixture which did not contain $Ir(2\text{-nqo})_3$.

Similarly nitrosation of 2-naphthol (3.00g, 20.8 mmol) gave unreacted 2-naphthol (26%) and 1,2-naphthoquinone 2-oxime (5%) (identical tlc and ir with an authentic sample). Tlc of the filtrate indicated a multicomponent mixture which did not contain $Ir(2\text{-nqo})_3$.

7.4.10 The system tris(1,2-naphthoquinone mono-oximato) rhodium(III)-pyridine

Tris(1,2-naphthoquinone 1-oximato) rhodium(III) (0.50g) was heated in pyridine (30 cm^3) under reflux for 7 days. The mixture on drying at 100°C/0.1mm afforded tris(1,2-naphthoquinone 1-oximato) rhodium(III) (95% recovery) (identified by tlc).

Similarly tris(1,2-naphthoquinone 2-oximato) rhodium(III) (0.50g) was recovered in approximately 95%.

7.4.11 The system tris(1,2-naphthoquinone mono-oximato) iridium(III)-pyridine

Tris(1,2-naphthoquinone 1-oximato) iridium(III) (0.50g) was heated in pyridine (30 cm^3) under reflux for 7 days. The mixture on drying at 100°C/0.1mm afforded tris(1,2-naphthoquinone 1-oximato) iridium(III) (95% recovery) (identified by tlc).

Similarly tris(1,2-naphthoquinone 2-oximato) iridium(III) (0.50g) was recovered in approximately 95%.

7.4.12 The system tris(1,2-naphthoquinone mono-oximato) rhodium(III)-triphenylphosphine

Tris(1,2-naphthoquinone 1-oximato) rhodium(III)

(0.50g) was added to a solution of triphenylphosphine (1.50g) in toluene (50 cm^3) for 7 days. The mixture afforded tris(1,2-naphthoquinone 1-oximato) rhodium(III) (ca. 95% recovery) (identified by tlc).

Similarly tris(1,2-naphthoquinone 2-oximato) rhodium(III) was recovered in ca. 95%.

7.4.13 The system tris(1,2-naphthoquinone mono-oximato) rhodium(III)-triphenylphosphine

Tris(1,2-naphthoquinone 1-oximato) iridium(III) (0.50g) was added to a solution of triphenylphosphine (1.50g) in toluene (50 cm^3) for 7 days. The mixture afforded tris(1,2-naphthoquinone 1-oximato) iridium(III) (ca. 95% recovery) (identified by tlc).

Similarly tris(1,2-naphthoquinone 2-oximato) iridium(III) was recovered in ca. 95%.

7.4.14 The system tris(1,2-naphthoquinone mono-oximato) rhodium(III)-hydrochloric acid

Tris(1,2-naphthoquinone 1-oximato) rhodium(III) (0.50g) was heated in concentrated hydrochloric acid (20 cm^3) for 3 days. The mixture was extracted with dichloromethane using a continuous extraction apparatus. Removal of the solvent from the extract gave tris(1,2-naphthoquinone 1-oximato) rhodium(III) (ca. 95% recovery) (identified by tlc).

Similarly tris(1,2-naphthoquinone 2-oximato) rhodium(III) was recovered in ca. 95%.

7.4.15 The system tris(1,2-naphthoquinone mono-oximato) iridium(III)-hydrochloric acid

Tris(1,2-naphthoquinone 1-oximato) iridium(III) (0.50g) was heated in concentrated hydrochloric acid (20 cm^3) for 3 days. The mixture was extracted with dichloromethane using a continuous extraction apparatus. Removal of the solvent from the extract gave tris(1,2-naphthoquinone 1-oximato) rhodium(III) (ca. 95% recovery) (identified by tlc).

Similarly tris(1,2-naphthoquinone 2-oximato) iridium(III) was recovered in ca. 95%.

7.4.16 Crystal preparation

Chloroiridic acid (3.5 cm^3), reduced with isopropanol (1 cm^3), was added to a solution of 1,2-naphthoquinone-1-oxime (5.80g) in methanol (150 cm^3) and heated to reflux for 3 days. Removal of solvent gave a brown solid which was treated with pyridine (excess) for 2 days. The mixture was filtered to give a small amount of purple solid. Recrystallisation of the solid from hot methanol gave needle-like crystals.

7.4.17 Reaction of cobalt(III) chloride hexahydrate with nitroso-R-salt

A solution of cobalt(III) chloride (1.00g; 4.2 mmol) in water (50 cm^3) was added to a solution of nitroso-R-salt (4.75g; 12.51 mol) in water (150 cm^3). The mixture was allowed to stir for 24h. Removal of water gave a red solid which was dried at 100°C/0.1mm Hg. The product was mixed with silica and the mixture washed

with methanol. Removing the methanol gave tris(1,2-naphthoquinone 1-oximato) cobalt(III). Analysis and yield are given in Table 7.1.

7.4.18 Reaction of rhodium(III) chloride hydrate with nitroso-R-salt

A solution of hydrated rhodium(III) chloride (2.00g; 4.0 mmol) in water (50 cm^3) was added to a solution of nitroso-R-salt (5.01g; 13.2 mmol) in water (150 cm^3). The mixture was heated for 3h to give an orange solution. The volume was reduced to 50 cm^3 to give a red solid. The solid was mixed with silica,dried at 100 C/0.1mmHgand extracted with methanol. Concentration of the solution gave red crystals which were filtered, dried to give tris(1,2-naphthoquinone 1-oximato-3,6-disulphonic acid; sodium salt) rhodium(III). Analysis and yield are given in Table 7.1.

7.4.19 Reaction of copper(II) chloride with nitroso-R-salt

A solution of copper(II) chloride dihydrate (2.00g;11.8 mmol)in water (50 cm^3) was added to a solution of nitroso-R-salt (6.01g; 16.5 mmol) in water (300 cm^3). The mixture gave a brown precipitate and filtered to give a brown solid and washed thoroughly with aqueous methanol and dried at 100 °C/0.1mmHg.The solid was coated in silica, washed with aqueous methanol. The brown solid was recovered by washing with hot distilled water. Removal of water gave a brown solid which was dried at 100°C/0.1mmHg. Analysis and yield are given in Table 7.1.

7.4.20 Reaction of iron(II) chloride hexahydrate with nitroso-R-salt

A solution of iron(II) chloride, hexahydrate (1.00g; 5.1 mmol) in water (50 cm^3) was added to a solution of nitroso-R-salt (5.80g; 15.5 mmol) in water (100 cm^3). A brown/yellow solution was immediately formed. The mixture was allowed to stir for 3 h and the water was removed. The dark green solid obtained was mixed with silica and the mixture was extracted with methanol. Removal of the solvent gave a green mono(1,2-naphthoquinone 1-oximato-3,6-disulphonic acid) iron(II). Analysis and yield are given in Table 7.1.

7.4.21 Reaction of iron(III) chloride hexahydrate with nitroso-R-salt

A solution of iron(III) chloride, hexahydrate (1.00g; 3.1 mmol) in water (50 cm^3) was added to a solution of nitroso-R-salt (4.19g; 11.7 mmol) in water (100 cm^3). A brown solution was immediately formed. The mixture was allowed to stir for 3 h and the water was removed. The brown/green solid obtained was mixed with silica and the mixture was extracted with methanol. Removal of the solvent gave a green mono(1,2-naphthoquinone 1-oximato-3,6-disulphonic acid) iron(II). Analysis and yield are given in Table 7.1.

7.4.22 Reaction of iron(II) ammonium sulphate hexahydrate with nitroso-R-salt

A solution of iron(II) ammonium sulphate (1.00g; 2.6

mmol) in water (50 cm^3) was added to a solution of nitroso-R-salt (3.25g; 8.5 mmol) in water (100 cm^3). The mixture, a green colour, was immediately formed and the mixture was allowed to stir for 5 h. The solvent was removed to give a green solid which was mixed with silica. The coated silica was then extracted with methanol. The methanol was removed to give a green bis(1,2-naphthoquinone 1-oximato) iron(II). Analysis and yield are given in Table 7.1.

7.4.23 Reaction of nickel(II) chloride with nitroso-R-salt

A solution of nickel(II) chloride hexahydrate (1.00g; 4.2 mmol) in water (50 cm^3) was added to a solution of nitroso-R-salt (4.75g; 12.6 mmol) in water (100 cm^3). A brown colour was immediately formed and the mixture was allowed to stir for 5 h. Removal of water gave a brown solid which was coated in silica. The coated silica was extracted with methanol. The methanol was removed from the extract to give a brown solid which was dried at 70°C/30 mmHg. Analysis and yield are given in Table 7.1.

7.4.24 Interaction of Cu(nRs Na).$10H_2O$ with pyridine

Cu(nRs Na).$10H_2O$ (0.6g) was stirred in excess pyridine (50 cm^3) for 2 d. To the mixture was added anhydrous diethyl ether. A brown solid was precipitated. This was thoroughly washed with ether and then methanol and dried at 70°C at 60 mmHg. Analysis and yield are given in Table 7.1.

Table 7.1 Analytical data for complexes of 1,2-naphthoquinone-3,6-disulphonic acid

	Found						Calculated						Yield %
	C	H	N	M	Na	S	C	H	N	M	Na	S	
Nitroso-R-salt	30.09	1.75	3.35		12.22	17.01	31.83	1.06	3.71	16.98	12.73	16.98	-
$Co(nRsNa_2)_3\ 5H_2O$	28.99	1.35	3.45	5.01	11.44	16.13	29.41	1.48	3.43	4.90	11.27	15.67	65
$Rh(nRsNa_2)_3 3H_2O$	28.29	1.07	2.98	7.96	10.92	16.08	29.24	0.98	3.41	8.36	11.69	15.59	33
$Ni(nRsHNa)_2 5H_2O$	29.33	2.03	3.01	7.03	5.99	14.78	29.82	2.24	3.48	7.33	5.72	15.90	42
Cu(nRs Na).$10H_2O$	21.10	3.42	2.88	10.31	4.33	11.01	20.10	4.02	2.35	10.72	3.85	10.72	33
Fe(nRs Na).$5H_2O$	25.73	2.51	2.69	10.01	4.91	12.31	24.05	3.21	2.81	9.35	4.61	12.83	46
$[NH_4]_2[Fe(nRs\ Na)_2]2H_2O$	28.31	2.97	6.68	7.10	3.25	15.01	28.92	2.39	6.75	6.75	5.54	15.42	59
$Cu(nRs\ Na)(py)_2(H_2O)_2$	39.83	2.11	6.81	9.89	3.48	10.01	40.75	2.43	7.13	10.86	3.91	10.86	47

7.4.25 Separation of rhodium from iridium with 1,2-naphthoquinone 1-oxime

a) *Effect of heating time*

A solution of rhodium (III) (50mg) and iridium (III) (50mg) in HCl (1:10) was adjusted to a pH 5.0 - 5.6 by adding NaOH and Na(OAc). This was added to a suspension of 1-nqoH (500mg) and stirred under conditions specified in Table 5.2 (Chapter 5). The mixture was filtered to give a brown solid and a dark brown filtrate. The filtrate was analysed by AAS to determine the amount of rhodium and iridium in solution.

b) *Effect of amount of reagent used*

A solution of rhodium (III) (50mg) and iridium (III) (50mg) in HCl (1:10) was adjusted to a pH 5.0 - 5.6 by adding NaOH and Na(OAc). This was added to a suspension of 1-nqoH and stirred under conditions specified in Table 5.3 (Chapter 5). The mixture was filtered to give a brown solid and a dark brown filtrate. The filtrate was analysed by AAS.

c) *Effect of pH*

A solution of rhodium (III) (50mg) and iridium (III) (50mg) in HCl (1:10) was added to a suspension of 1-nqoH (500mg) in water (50ml) for 1.5h at reflex termperature (Table 5.4, Chapter 5). The mixture was filtered to give a solid and a dark brown filtrate. The filtrate was analysed by AAS.

7.4.26 Extraction of rhodium using Esso Solvesso 200 or Shellsol

The solid (0.5g) obtained from the above reactions was stirred in Esso Solvesso 200 (100 cm^3) for 1 d. The mixture was filtered and the filtrate analysed by AAS. The analysis indicated a solubility of 2 - 2.5g/litre. When Shellsol was used the solubility was determined to be only 0.1g/litre.

7.4.27 Interaction of organic rhodium with sodium sulphide

The rhodium complex (1.00g) was treated with sodium sulphide (20%) (50cm^3) and the mixture boiled for 5 h. The mixture was filtered to give a black solid residue (0.90g). The filtrate was analysed by AAS and found to contain 2.75mg of rhodium.

7.4.28 Recovery of rhodium metal

The black solid residue (0.5g) obtained from reaction 7.4.27 was stirred in NaOH (5%) (50 cm^3) for 1 h and then filtered. The solid recovered was ignited at 700° for 1 h. The residue was reduced under hydrogen to give a rhodium powder (0.41g) of 99.2% purity.

The black solid residue (0.5g) was stirred in in NaOH (5%) (50 cm^3) for 1 h and then filtered. The solid recovered was ignited at 700° for 1 h. The residue was then stirred in $HCl:H_2O$ (1:1) (50 cm^3) for 2 d in the presence of Cl_2 gas to give a rose-red solution. Formic acid (2 cm^3) was added to the solution and heated to

reflux. Rhodium metal precipitated which was then ignited and reduced in a hydrogen atmosphere to give rhodium (0.42g) of 99.3% purity.

7.5 Oxidation reactions

Catalytic oxidation of catechols

The metal catalyst in aqueous methanol (20cm^3) and catechol in methanol (100cm^3), pyridine(100cm^3), pyridine/methanol 100cm^3(30:70) toluene (100cm^3) or tetrahydrofuran(100 cm^3) were stirred at room temperature in an oxygen atmosphere in quantities specified in Table 7.2 for 200 h. The solvents were removed under pressure and then extracted with ether. To the ether extract was added NaOH (5%) (5 cm^3) and the aqueous layer was separated. The ether extract was evaporated and residue was chromatographed on silica gel using toluene and dichloromethane. The products were recrystallised from hexane and were identified by i.r. and m.s. with those in the literature.(**Chapter 6**)

The aqueous layer was titrated with HCl (5%) and the amount required to neutralise was less than amount of alkali used. Attempt to recrystallise and separate the residue component was unsuccessful.

When the reactions were carried out in air no oxidation occurred.

The reactions were monitored by taking samples at intervals and analysed for oxidation products by glc, tlc and ir spectroscopy. The yield of the products was determined by glc (5% Carbowax 20M on chromosorb W;HP).

Table 7.2 Catalytic oxidations of 3,5-di-tert-butylcatechol

Aerobic oxidation of 3,5-di-tert-butylcatechol at 20°C after 200 h using Fe(nRs Na)$5H_2O$

Catalyst (g)	Catechol (g)	Oxidation products (%)			
		1	2	3	4
0.05	5.0	30	16	18	-
0.10	5.0	33	15	23	-
0.15	5.0	36	18	25	-
0.20	5.0	39	17	21	-
0.25	5.0	39	19	26	-
0.50	5.0	40	23	24	-
1.00	5.0	40	21	28	3

Aerobic oxidation of 3,5-di-tert-butylcatechol at 20°C after 200 h using Cu(nRs Na)$10H_2O$

Catalyst (g)	Catechol (g)	Oxidation products (%)			
		1	2	3	4
0.10	5.0	16		24	8
0.20	5.0	16		26	8
0.30	5.0	18		28	9
0.50	5.0	19		28	10
1.00	5.0	20		28	10

1 = 3,5-Di-tert-butyl muconic acid anhydride
2 = 3,5-Di-tert-butyl 2H-Pyran-2-one
3 = 3,5-Di-tert-butyl-1,2-benzoquinone
4 = Unidentified acidic product

Table 7.2 continued

Aerobic oxidation of 3,5-di-tert-butylcatechol using Fe(nRs Na)$5H_2O$ in the presence of pyridine, toluene and tetrahydrofuran

Catalyst (g)	Catechol (g)	Solvent	Oxidation products (%)			
			1	2	3	4
0.10	5.0	Methanol	34	16	21	-
0.10	5.0	Pyridine/ methanol	37	20	25	-
0.10	5.0	Excess pyridine	NR	NR	NR	-
0.10	5.0	Tetrahydrofuran	18	8	13	-

Aerobic oxidation of 3,5-di-tert-butylcatechol using Cu(nRs Na)$10H_2O$in the presence of pyridine, toluene and tetrahydrofuran

Catalyst (g)	Catechol (g)	Solvent	Oxidation products (%)			
			1	2	3	4
0.1	5.0	Methanol	17	-	26	9
0.1	5.0	Pyridine/ methanol	21	-	28	13
0.1	5.0	Excess pyridine	NR	NR	NR	NR
0.1	5.0	Toluene	11	-	16	6
0.1	5.0	Tetrahydrofuran	12	-	14	8

1 = 3,5-Di-tert-butyl muconic acid anhydride
2 = 3,5-Di-tert-butyl 2H-Pyran-2-one
3 = 3,5-Di-tert-butyl-1,2-benzoquinone
4 = Unidentified acidic product

Table 7.2 continued

Aerobic oxidation of 4-tert-butylcatechol at 20°C after 200 h

Catalyst (g)	Catechol (g)	Solvent	Oxidation products (%) 1	2	3	4
Fe(nRs Na) (0.1g)	5.0	Methanol	23	10	8	
Fe(nRs Na) (0.1g)	5.0	Methanol/ pyridine	25	13	9	
Cu(nRs Na) (0.1g)	5.0	Methanol	18	9	-	7
Cu(nRs Na) (0.1g)	5.0	Methanol/ pyridine	23	12	-	9

1 = 4-tert-Butyl-1,2-benzoquinone
2 = 4-tert-Butylmuconic acid anhydride
3 = 4-tert-Butyl-2H-pyran-2-one
4 = Unidentified acidic component

Aerobic oxidation of catechol at 20°C after 200 h

Catalyst (g)	Catechol (g)	Solvent	Oxidation products (%) 1	2	3	4
Fe(nRs Na) (0.1g)	5.0	Methanol	19	10	6	-
Fe(nRs Na) (0.1g)	5.0	Methanol/ pyridine	22	13	8	-
Cu(nRs Na) (0.1g)	5.0	Methanol	17	-	10	7
Cu(nRs Na) (0.1g)	5.0	Methanol/ pyridine	19	12	-	9

1 = 1,2-Benzoquinone
2 = Muconic acid anhydride
3 = 2H-pyran-2-one
4 = Unidentified acidic component

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